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Pyro Solution

Dry Pyro —	4 Drams
Brom. Amm. —	20 Grains
Sodium Sulph.	327 "
Citric Acid —	2 "
Water —	5 Oz

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A MANUAL

OF

PHOTOGRAPHIC CHEMISTRY.

Page A Developer

1 Oz Ovoir Pyro. —— 1. Oz.
~~440 Gr~~. Brom. Amonia 80 Gr
~~1 Oz 60 Gr~~ Sodium Sulphite 2½ Oz
~~3 Pints of~~ Water 20 Oz.
Citric Acid a few crystals. 60 Gr.

To Develope

2 Drams of solution
12 Drams of water
5 Drops Amonia 880.

Gold Solution

1 Teas spoonful of Borax.
40 Drops of Gold Solution.

A MANUAL

OF

PHOTOGRAPHIC CHEMISTRY,

THEORETICAL AND PRACTICAL.

BY

REV. T. FREDERICK HARDWICH, M.A.

NINTH EDITION,

EDITED BY

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PREFACE

TO

THE NINTH EDITION.

SINCE the publication of the previous editions of this Manual, two changes of importance have occurred; the nomenclature and atomic weights of chemical compounds have to a great extent been altered, and the collodion process has, especially in England, been largely supplanted by gelatine emulsion.

It has, however, seemed judicious to the Editor of this edition neither to entirely discard the old nomenclature in favour of the new, nor to assume the collodion process to be defunct. For while the chemist of the present day knows that—to adduce the case of a familiar body — the substance expressed by the formula $Na_2S_2O_3 + 5$ Aq. is *Thio-Sulphate of Soda*, there is scarcely one among thirty photographers or dealers in photographic chemicals who is aware that this is the modern term to express Hyposulphite of Soda. Hence a work, intended to be of every-day use to photographers, would have its value impaired by the exclusive use of terms as yet imperfectly understood.

Again, an edition of "Hardwich's Manual," devoid of the invaluable researches of Mr. Hardwich in the collodion process, would indeed be an anomaly, hence the Editor has restored as fully as possible the teachings

of this *savant* on this topic, subject to the alteration of the chemical notation and equivalents to the requirements of the present time. It is worthy of notice that notwithstanding the prevalent employment of gelatine plates, the manufacture of collodion continues almost unaffected. The Editor is informed by one firm, presumably the most extensive collodion manufacturers in the world, that so far from there being any stagnation in that department, at no time in their business career has there been such a demand for collodion.

The Chapters on the Optics of Photography, and on the Emulsion and other negative and printing processes, will be found to be brought up to the present time.

To Mr. W. B. Bolton, Mr. E. W. Foxlee, and others, the Editor tenders his acknowledgments for information and services of a specialistic nature.

J. Traill Taylor,

December, 1882. *Editor.*

CONTENTS.

CHAP.		PAGE
	HISTORICAL SKETCH OF EARLY PHOTOGRAPHY . .	1
I.	OUTLINES OF GENERAL CHEMISTRY	9
II.	VOCABULARY OF PHOTOGRAPHIC CHEMICALS . . .	29
III.	THE SALTS OF SILVER EMPLOYED IN PHOTOGRAPHY.	102
IV.	ON THE DEVELOPMENT OF AN INVISIBLE IMAGE BY MEANS OF A REDUCING AGENT	117
V.	FIXING AGENTS	145
VI.	THE MANUFACTURE OF PHOTOGRAPHIC COLLODION .	151
VII.	THE CHEMISTRY OF THE NITRATE BATH	178
VIII.	ON POSITIVE AND NEGATIVE COLLODION PHOTOGRAPHS	186
IX.	ON THE THEORY OF POSITIVE PRINTING	219
X.	THE PHOTOGRAPHIC DARK ROOM	263
XI.	FORMULÆ FOR NEGATIVE SOLUTIONS	265
XII.	MANIPULATIONS OF THE WET COLLODION PROCESSES .	274
XIII.	THE POSITIVE COLLODION PROCESS ON GLASS OR METALLIC PLATES (FERROTYPES)	281
XIV.	THE NEGATIVE COLLODION PROCESSES ON GLASS . .	284
XV.	PORTRAITURE.—POSITIVE AND NEGATIVE	296
XVI.	PHOTOGRAPHIC ENLARGEMENTS	302

CHAP.		PAGE
XVII.	THE PRACTICAL DETAILS OF PHOTOGRAPHIC PRINTING	316
XVIII.	THE GELATINE EMULSION PROCESS	365
XIX.	THE COLLODION EMULSION PROCESS	383
XX.	WILLIS'S PROCESS FOR ENGINEERS' PLANS	385
XXI.	MICRO-PHOTOGRAPHY	388
XXII.	THE OPTICS OF PHOTOGRAPHY	392
XXIII.	ON BINOCULAR VISION AND THE STERESOCOPE	425
XXIV.	CHROMOTYPE OR LAMBERTYPE	436
	APPENDIX	445

HISTORICAL SKETCH

OF

EARLY PHOTOGRAPHY.

The Art of Photography, which has now attained such perfection, and has become so popular amongst all classes, is one of comparatively recent introduction.

The word Photography means literally "writing by means of Light;" and it includes all processes by which any kind of picture can be obtained by the chemical agency of Light, without reference to the nature of the sensitive surface upon which it acts.

The philosophers of antiquity, although chemical changes due to the influence of Light were continually passing before their eyes, do not appear to have directed their attention to them. Some of the *Alchemists* indeed noticed the fact that a substance termed by them "Horn Silver," which was Chloride of Silver which had undergone fusion, became *blackened* by exposure to Light; but their ideas on such subjects being of the most erroneous nature, nothing resulted from the discovery.

The first philosophical examination of the decomposing action of Light upon compounds containing Silver was made by the illustrious Swedish chemist, Scheele, in the year 1777. It was remarked by him that the maximum chemical or decomposing effect of the spectrum lay near the *violet* part and gradually diminished towards the red. He also attributed the blackening of Chloride of Silver by light to the libera-

tion of Chlorine and the formation of Hydrochloric acid. Both these statements have been proved to be true. Scheele's experiments terminated here, but they do not seem to have attracted that attention which they deserved. In fact, they were looked upon as more curious than useful.

Earliest application of these Facts to purposes of Art.—The first attempts to render the blackening of Silver Salts by Light available for artistic purposes were made by Wedgwood and Davy, and published in 1802. But it is evident that the experiments must have been made several years previously, as Wedgwood had been dead several years before that date. A sheet of white paper or of white leather was saturated with a solution of Nitrate of Silver, and the *shadow* of the figure intended to be copied projected upon it. Under these circumstances the part on which the shadow fell remained white, whilst the surrounding exposed parts gradually darkened under the influence of the sun's rays.

Unfortunately, these and similar experiments, which appeared at the outset to promise well, were checked by the experimentalists being unable to discover any means of fixing the pictures, so as to render them indestructible by diffused Light. The unchanged Silver Salt being permitted to remain in the white portions of the paper, naturally caused the proofs to blacken in every part, unless carefully preserved in the dark.

It is singular that these distinguished philosophers, finding *leather* to be the most sensitive medium, did not hit on the cause—viz., Tannin or Gallic acid.

The sensitive surfaces employed by Wedgwood and Davy could not be impressed in the Camera, although, it would appear, the attempt was made. Davy, however, succeeded in getting a faint impression in the solar microscope, where the image was much condensed in size.

Wedgwood and Davy's plan of throwing the shadow of the object to be copied on to a medium sensitive to

Light forcibly reminds us of the origin of Portrait painting as given by an ancient Roman writer:

"Corinthi puella, capta amore juvenis, illo abeunte peregre, umbram ex facie ejus ad lucernam in pariete lineis circumscripsit. Talis picturæ fuit origo."

Whether this was the origin of painting or not is a matter which cannot now be determined; but we know, from authentic evidence, that this was exactly the plan adopted by Wedgwood and Davy in their earlier experiments on Photography. The only difference is, that these eminent Philosophers used *Nature's pencil* to delineate the object, and not a crayon worked by hand.

Introduction of the Camera Obscura, and other Improvements in Photography.—The "Camera Obscura," or darkened chamber, by means of which a luminous image of an object may be formed, was invented by Baptista Porta, of Padua; but the preparations employed by Wedgwood were not sufficiently sensitive to be easily affected by the subdued light of that instrument.

In the year 1814, however, twelve years subsequent to the publication of Wedgwood's paper, M. Niépce, of Châlons, having directed his attention to the subject, succeeded in perfecting a process in which the Camera could be employed, although the sensibility was still so low that an exposure of some hours was required to produce the effect.

In the process of M. Niépce, which was termed "Heliography," or "sun-drawing," the use of the Silver Salts was discarded, and a resinous substance, known as "Bitumen of Judæa," substituted. This resin was smeared on the surface of a metal plate, and exposed to the luminous action. The light in acting upon it so changed its properties, that it became *insoluble* in certain essential oils. Hence, on subsequent treatment with the oleaginous solvent, the *shadows* dissolved away, and the *lights* were represented by the unaltered resin remaining on the plate.

There are several specimens of Niépce's original process in the British Museum; some of which also show his attempts at etching by the same process.

The Discoveries of M. Daguerre.—MM. Niépce and Daguerre appear at one time to have been associated as partners, for the purpose of mutually prosecuting their researches; but it was not until after the death of the former,—viz., in 1839—that the process named the Daguerreotype was given to the world. Daguerre was dissatisfied with the slowness of action of the Bitumen sensitive surface, and directed his attention mainly to the use of the Salts of Silver, which are thus again brought before our notice.

Even the earlier specimens of the Daguerreotype, although far inferior to those subsequently produced, possessed a beauty which had not been attained by any Photographs prior to that time.

The sensitive plates of Daguerre were prepared by exposing a silvered tablet to the action of the vapour of *Iodine*, so as to form a layer of Iodide of Silver upon the surface. By a short exposure in the Camera an effect was produced, not visible to the eye, but appearing when the plate was subjected to the vapour of Mercury. This feature,—viz., the production of a *latent* image upon Iodide of Silver, with its subsequent development by a chemical reagent,—is one of the first importance. Its discovery at once reduced the time of taking a picture from hours to minutes, and promoted the utility of the Art.

Daguerre also succeeded in partially fixing his proofs by removal of the unaltered Iodide of Silver from the shadows; but it was not till some years afterwards that attention was called to Herschel's researches on the Hyposulphites. These contributions to Chemical science were published in the course of the year 1821, in "The Edinburgh Philosophical Journal." He not only investigated the Chemical composition of the soluble Hyposulphites, but also their power of dissolving the Haloid Salts of Silver, within certain limits,

when double salts were formed. These also he chemically formulated and described. Strange as it may appear, Herschel's discoveries escaped the attention of our early Daguerreotypists and workers by the Talbotype process.

On a Means of Multiplying Photographic Impressions, and other Discoveries of Mr. Fox Talbot.—The first communication made to the Royal Society by Mr. Fox Talbot, in January, 1839, related to the preparation of a more sensitive paper than had been previously known, and also to a method of fixing the pictures by common Salt. It was directed that the paper should be first dipped in Solution of Chloride of Sodium, and then in Nitrate of Silver. By proceeding in this way a white substance termed *Chloride of Silver* is formed, more sensitive to light than the Nitrate of Silver originally employed by Wedgwood and Davy. The object is laid in contact with the prepared paper, and being exposed to light, a copy is obtained, which is *Negative*, —*id est*, with the light and shade reversed. The discovery of a way of fixing these Negatives was of great importance, as it not only rendered them unalterable by light, but it further allowed of their being used to obtain copies having the light and shade correct, or *Positive* copies, which was effected by laying the Negative over a second sheet of prepared sensitive paper, so as to allow the sun's light to pass through the transparent parts. Under these circumstances, when the Negative is raised, a natural representation of the object is found below, the tints having been again reversed by the second operation.

This production of a Negative Photograph, from which any number of Positive copies may be obtained, is a cardinal point in Mr. Talbot's invention, and one of great importance.

Another most important discovery was that of the existence of an invisible image impressed on the paper by a much shorter exposure to light than was necessary to produce a visible one, and capable of being after-

wards rendered visible. Mr. Talbot took out a patent for a process of this kind in 1841. Mr. Brayley had, however, as early as 1839, described in a lecture at the London Institution a similar method communicated to him by the Rev. J. B. Reade. Mr. Talbot's process was, however, a decided advance on the former, in consequence of his employing Acetic Acid to check action not due to light. In this process, a sheet of paper is first coated with Iodide of Silver by soaking it alternately in Iodide of Potassium and Nitrate of Silver; it is then washed with solution of Gallic Acid, containing Nitrate of Silver and Acetic Acid (sometimes termed *Gallo-Nitrate of Silver*), by which the sensibility to light is greatly augmented. An exposure in the Camera of some seconds or minutes, according to the brightness of the light, impresses an invisible image, which is brought out by treating the plate with a fresh portion of the mixture of Gallic Acid, Nitrate of Silver, and Acetic Acid employed in exciting.

On the Use of Glass Plates to retain Sensitive Films.—The principal defects in the Calotype process are attributable to the coarse and irregular structure of the fibre of paper, even when manufactured with the greatest care, and expressly for Photographic purposes. In consequence of this, the same amount of exquisite definition and sharpness of outline as that resulting from the use of metal plates cannot be obtained.

We are indebted to Sir John Herschel for the first employment of glass plates to receive sensitive Photographic films.

The Iodide of Silver may be retained upon the glass by means of a layer of Albumen or white of egg, as proposed by M. Niépce de Saint-Victor, nephew to the original discoverer of the same name.

A more important improvement still was the employment of "Collodion" for a similar purpose.

Collodion is an ethereal solution of Pyroxyline, a feebly explosive variety of Gun-cotton. On evaporation it leaves a transparent layer, resembling gold-

beater's skin, which adheres to the glass with some tenacity. M. Le Grey, of Paris, originally suggested that this substance might perhaps be rendered available in Photography, but our own countryman, the late Mr. F. S. Archer, was the first to carry the idea out practically. In a communication to "The Chemist," in the autumn of 1851, this gentleman gave a description of the Collodion process much as it now stands; at the same time proposing the substitution of *Pyro*-gallic Acid for the Gallic Acid previously employed in developing the image.

At that period no idea could have been entertained of the stimulus which this discovery would render to the progress of the Art; but experience has now abundantly demonstrated that, as far as all qualities most desirable in a Photographic process are concerned, except in extreme sensitiveness, none at present known can excel, or perhaps equal, the Collodion process.

Parallel with the above Photographic discoveries were others in a different direction, and these, at the present day, are exercising a vast influence on commercial Photography. In the year 1839, Mr. Mungo Ponton announced to "The Royal Scottish Society of Arts" that Bichromate of Potash might be used to sensitize paper. The parts exposed to light became of a dark orange tint, which was insoluble in water; while the yellow colour, not acted on by light, could be removed by washing in water.

The full significance of this discovery was not appreciated till Mr. Fox Talbot afterwards showed that it was only in combination with organic matter that this salt was sensitive to light at all. In the year 1852 he took out a patent for the use of a Bichromate and Gelatine for a new process of engraving on steel. This is the foundation of almost all the Photo-engraving and Photo-lithographic processes of the present day, besides others of still greater importance in Photographic printing.

In 1855 M. Poitevin patented a Carbon printing

process founded on this principle. He dabbed over a sheet of paper a mixture of Bichromate of Potash, Gum Arabic, and finely divided Charcoal. When dry, it was exposed to light under a negative, and then placed in water. The parts unacted on by light were washed away, leaving the white paper exposed. The rest remained unchanged. This was the first Carbon-printing process, by which, by judicious improvements, permanent pictures of great beauty are now produced.

When a large number of prints are required, the Collotype and Woodbury processes, which have now reached a high state of perfection, afford the means of producing them suitable for book illustration. By these methods the half-tones of a Negative are most perfectly rendered, while the rapidity of production is vastly increased.

These remarks have been confined to what may be designated the early history of Photography.

OUTLINES

OF

GENERAL CHEMISTRY.

CHAPTER I.

All substances with which we are acquainted, whether solid, liquid, or gaseous, are either elements, or compounds of elements, or mixtures of elements, or mixtures of compounds. It is necessary, in the first place, to understand these terms clearly.

ELEMENTS.

An Element is a substance which consists of one kind of matter only, or which has never yet been decomposed or separated into two or more kinds of matter. The number of such simple substances at present known is 64; the names, symbols, and atomic weights are given in the following table, and it will be observed that both in respect of the number of elementary bodies given and the atomic weights or combining proportions, the table here given is more comprehensive than those in former editions of this work.

In this table the most important Elements are printed in a more conspicuous type than those of which less is known, or which are of less present importance. Those names to which an asterisk is affixed are non-metallic Elements, the others not so distinguished are Metals.

TABLE OF ELEMENTARY BODIES WITH THEIR SYMBOLS AND ATOMIC WEIGHTS.

Name.	Symbol.	Atomic Weight.	Name.	Symbol.	Atomic Weight.
ALUMINIUM	Al	27·4	Molybdenum	Mo	96
Antimony (Stibium)	Sb	122	Nickel	Ni	58·8
Arsenic	As	75	Niobium	Nb	94
Barium	Ba	137	**NITROGEN***	N	14
Beryllium	Be	9·4	Osmium	Os	199·2
Bismuth	Bi	210	**OXYGEN***	O	16
Boron*	B	11	Palladium	Pd	106·6
BROMINE*	Br	80	**PHOSPHORUS***	P	31
Cadmium	Cd	112	**PLATINUM**	Pt	197·4
Cæsium	Cs	133	**POTASSIUM** (Kalium)	K	39·1
CALCIUM	Ca	40	Rhodium	Rh	104·4
CARBON*	C	12	Rubidium	Rb	85·4
Cerium	Ce	92	Ruthenium	Ru	104·4
CHLORINE*	Cl	35·5	Selenium*	Se	79·4
Chromium	Cr	52·2	**SILICIUM***	Si	28
Cobalt	Co	58·8	**SILVER** (Argentum)	Ag	108
COPPER (Cuprum)	Cu	63·4	**SODIUM** (Natrium)	Na	23
Davyum	Da		Strontium	Sr	87·6
Didymium	D	95	**SULPHUR***	S	32
Erbium	E	112·6	Tantalum	Ta	182
FLUORINE*	F	19	Tellurium*	Te	128
Gallium	Ga	68	Thallium	Tl	204
Gold (Aurum)	Au	197	Thorinum	Th	235
HYDROGEN*	H	1	**TIN** (Stannum)	Sn	118
Indium	In	113·4	Titanium	Ti	50
IODINE*	I	127	Tungsten, or Wolfram	W	184
Iridium	Ir	198	Uranium	U	240
IRON (Ferrum)	Fe	56	Vanadium	V	51·2
Lanthanum	La	93·6	Yttrium	Y	61·7
LEAD(Plumbum)	Pb	207	**ZINC**	Zn	65·2
Lithium	Li	7	Zirconium	Zr	89·6
Magnesium	Mg	24			
MANGANESE	Mn	55			
MERCURY (Hydrargyrum)	Hg	200			

TABLE OF SYMBOLS OF THE MORE IMPORTANT COMPOUNDS USED IN PHOTOGRAPHY.

NAME.	SYMBOL.	
Acid, Acetic (Cryst.)	$H,C_2H_3O_2$	60
,, Citric	$H_3C_6H_5O_7+H_2O$	210
,, Formic	H,CHO_2	46
,, Gallic	$H,C_7H_5O_5$	170
,, Hydriodic	HI	128
,, Hydrobromic	HBr	81
,, Hydrochloric	HCl	36·5
,, Hydrocyanic	HCN	27
,, Hydrosulphuric (Sulph. Hydro)	H_2S	34
,, Nitric	H,NO_3	63
,, Pyrogallic	$H_3C_6H_3O_3$	126
,, Sulphuric	HSO_4	98
,, Tannic	$C_{14}H_{10}O_9$	322
Alcohol	C_2H_6O	46
Ammonical Gas	NH_3	17
Ammonium, Bromide	NH_4Br	98
,, Chloride	NH_4Cl	53·5
,, Iodide	NH_4I	145
,, Nitrate	NH_4,NO_3	80
,, Sulphydrate of	NH_4,HS	51
,, Sulphocyanide of	NH_4,CNS	76
Barium, Chloride (Cryst.)	Ba,Cl_2+2H_2O	244
Baryta, Nitrate of	$Ba,(NO_3)_2$	261
Benzole	C_6H_6	78
Chloroform	CH,Cl_3	119·5
Cadmium, Bromide (Commer.)	Cd,Br_2+4H_2O	344
,, Iodide	CdI_2	366
Calcium Bromide (Cryst.)	$CaBr_2+4H_2O$	272
,, Chloride	$CaCl_2$	111
Ether	$C_4H_{10}O$	74
Gold, Terchloride	$AuCl_3$	302·5
Iron, Perchloride	Fe_2Cl_6	325
,, Iodide	FeI_2	310
,, Nitrate	$Fe(NO_3)_2+6H_2O$	288
,, Sulphate	$FeSO_4+7H_2HO$	278
,, Double Sulphate of Ammonia and	$FeSO_4,(NH_4)_2SO_4+6H_2O$	392
Lead, Acetate (Cryst.)	$Pb,(C_2H_3O_3)+{}_2H_2O$	343
,, Nitrate	$Pb,(NO_3)^2$	331
Lithium, Iodide	$LiI6H_2O$	242

TABLE OF SYMBOLS, &c.—*continued.*

Name.	Symbol.	
Lithium, Bromide	$LiBr$	87
Mercury, Chloride (Corrosive Sublimate)	$HgCl_2$	271
Mercury, Subchloride (Calomel)	Hg_2Cl_2	471
Potassium, Bichromate	$K_2Cr_2O_7$	294·6
,, Carbonate	K_2CO_3	138·2
,, Hydrate	KOH	56·1
,, Nitrate	KNO_3	101·1
,, Bromide	KBr	119·1
,, Chloride	KCl	74·6
,, Cyanide	KCN	65·1
,, Iodide	KI	166·1
Silver, Acetate	$AgC_2H_3O_2$	167
,, Bromide	$AgBr$	188
,, Carbonate	Ag_2CO_3	276
,, Chloride	$AgCl$	143·5
,, Hyposulphite	$Ag_2S_2O_3$	328
,, Iodide	AgI	235
,, Nitrate	$AgNO_3$	170
,, Oxide	Ag_2O	232
,, Sulphide	Ag_2S	248
Sodium, Acetate (Cryst.)	$NaC_2H_3O_2+6H_2O$	190
,, Carbonate (Cryst.)	$Na_2CO_3+10H_2O$	286
,, Hyposulphite (Cryst.)	$Na_2S_2O_3+5H_2O$	248
,, Nitrate	$NaNO_3$	85
,, Bromide	$NaBr$	103
,, Chloride	$NaCl$	58·5
,, Iodide	NaI	150
Uranium, Nitrate	$(UrO_2),(NO_3)^2+6H_2O$	384
Zinc, Bromide	$ZnBr_2$	225·2
,, Chloride	$ZnCl_2$	136·2

The Symbols attached to the elementary bodies are formed of the first letter of their Latin names, another letter being added to distinguish between two or more commencing with the same letter.

The atomic or combining weights may represent grains, ounces, pounds, or any other weight. On account of Hydrogen being the lightest of the known elementary bodies, it is taken as the unit of the scale, and the numeral 1 affixed to it.

COMPOUNDS AND MIXTURES.

These elementary substances are capable of uniting with each other to form Compounds, which differ from their elements in appearance and properties, the more completely that the latter were opposed to each other in their properties. Thus the gaseous element Chlorine is capable of combining with the metal Sodium, to form with it the well-known solid, common Salt, in which neither a gas nor a metal can be detected by the senses. The black solid, Iodine, unites with the metal Potassium, to form the white compound Iodide of Potassium. The two gases Oxygen and Hydrogen form by their union, the liquid, Water. Chemical combination is often attended with heat and light, the union of bodies with the Oxygen of the air, when accompanied with these phenomena, being termed combustion.

Mixture differs entirely from *Chemical combination*, in that it leaves the properties of the ingredients comparatively unchanged and perceptible to the senses, it is not attended with heat, excepting that which may be due to the friction used, and very simple means usually serve to separate the ingredients again. Thus, gunpowder is an example of the most perfect mixture of the three ingredients, Charcoal, Nitrate of Potash, and Sulphur; yet the sense of taste will detect the Nitre, the Sulphur may be discovered by the smell when rubbed, and the eye perceives the colour of the Charcoal. Sulphur and finely divided Iron might be so intimately mixed, that the two ingredients could not be separately distinguished by the eye, but the Iron might still be separated by a magnet from the Sulphur; if however true combination were brought about by the application of a gentle heat, a great increase of heat is suddenly perceived, and if the materials were in the right proportions, the magnet would no longer discover any Iron in the resulting compound. Hydrogen and Oxygen gases may be *mixed*, and they will remain gases still, but when *combined* the gaseous character is lost, and the liquid, water, results.

Of the compounds produced by the union of two elements, the class of *Oxides*, formed by the combination of Oxygen with another element, is the most important. These Oxides form three important classes, namely, Bases, Acids, and neutral Oxides, each of which must be separately considered.

BASES.

The Basic Oxides are found only among the *metallic* Oxides, although the whole of the metals do not furnish basic Oxides. The most perfect examples of Bases are the Oxides of Potassium, Sodium, Lithium, Barium, Calcium, Strontium, Magnesium; the Oxides of the first three, Potassium, Sodium, and Lithium, known as Potash, Soda, and Lithia, are distinguished from other bases by the term "Alkali;" the Oxides of the other four are known as "Alkaline" Earths. The Alkalies and Alkaline Earths exhibit all the true characteristics of bases in perfection—viz., causticity and corrosiveness, and the power of uniting with another class of compounds, the Acids, equally caustic and corrosive, and of producing compounds comparatively inactive and harmless, they possess also the property of changing the red of Litmus to blue, and the yellow of Turmeric to brown. The property of Litmus and Turmeric in changing colour with bases and acids has caused them to be used for "test-papers," which serve to detect an exceedingly minute amount of one of the stronger bases, or acids in a free state. The other metallic oxides termed bases exhibit the basic character in very variable degrees, some, such as the Oxides of Silver and Lead, "neutralize" the strongest acids perfectly, so that the product no longer affects test-paper; others, such as the Oxides of Zinc and Iron, neutralize acids, but imperfectly, so that the products of the combination always show an *Acid* reaction with test-paper.

ACIDS.

The most important of the Acid Oxides are those of non-metallic elements; only a few of the metals, as

Arsenic, Chromium, and Manganese, furnishing acid oxides. Some metals, as Chromium and Manganese, have both basic and acid oxides; when this is the case, the acid oxide always contains the most Oxygen.

Taking the Oxides of Nitrogen and Sulphur known as Nitric and Sulphuric Acids as types, the characteristics of acids may be stated to be, intense sourness and corrosiveness, the power of "neutralizing" the strongest bases, so that the product no longer affects test-paper, and the property of changing blue Litmus to red, even when extremely dilute. The acid oxides, like the bases, possess these characters in very different degrees, the weaker bases and acids approaching each other in character,—and in the same proportion, having little tendency to combine.

The stronger Oxygen Acids always retain, even in their concentrated state, a certain amount of water, which is essential to them. If deprived of this, they form what are termed "Anhydrides," which are essentially different from acids.

The modern theory of the Oxygen Acids is to consider them as Salts of Hydrogen in which the Hydrogen is replaced by a metal in combination. Thus—

$$HNO_3 + KHO = KNO_3 + H_2O.$$

Hydrogen Acids.—While speaking of acids, it may be as well to mention that besides the acids above alluded to, which are Oxides, there are others which contain no Oxygen, but are compounds of Hydrogen with certain elements, chiefly Chlorine, Bromine, Iodine, Fluorine, and Sulphur, and with certain compounds which perform many of the functions of these elements. These acids are distinguished by the prefix Hydro-, the rest of the name being derived from the other element of the acid; thus the compound of Chlorine and Hydrogen is termed Hydrochloric Acid, that of Hydrogen and Iodine, Hydriodic Acid. Most of these Hydrogen Acids are gaseous bodies, and the liquids known under their names are solutions of the same in water.

NEUTRAL OXIDES.

Besides forming Acid and Basic Oxides, Oxygen also unites in a few cases with elements to form neutral bodies which have no tendency to unite with either acids or bases. Such are two of the Oxides of Nitrogen, the Oxide of Carbon, and the black Oxide of Manganese.

SALTS.

The combination of an Acid with a Base produces what is termed a *Salt*. This class of compounds is a very large and important one, and includes many substances that would not ordinarily be recognized under that term. When the affinities of the acid and base of the salt are about equal, as is the case, for example, with Sulphuric Acid and Potash in Sulphate of Potash, the salt has no action on test-paper. In many cases however the reaction of the acid or base preponderates; thus Sulphate of Iron, a compound of a powerful acid with the weak base Oxide of Iron, always has an acid reaction: Carbonate of Soda, on the other hand, consists of a strong base and a feeble acid, the Carbonic, and therefore is always alkaline to test-paper. Both of these salts, though far from neutral in *reaction*, are yet neutral in *composition*.

Salts, derived from Oxygen Acids, always contain the whole of the acid and base, but with Hydrogen Acids the case is different; in these, the Hydrogen of the acid unites with the Oxygen of the base to form water, which separates on evaporation to dryness, and the other element of the acid unites with the metal of the base to form what is termed a "Haloid Salt," a name derived from ἁλς, ἅλος (Halos), Sea Salt, because common Salt, Chloride of Sodium, is a familiar example. This compound may be formed by the union of Hydrochloric Acid and Soda (Oxide of Sodium), and would be termed Hydrochlorate of Soda if it retained the acid and base entire, but as each is decomposed, one giving up its Hydrogen, and the other its Oxygen to form water,

which separates, the Chlorine of the acid and Sodium of the base alone remain, and the product of their combination is termed Chloride of Sodium, which contains no longer either acid or base, and yet is a true Salt. Examples of such salts are Iodides, Bromides, Fluorides, and Chlorides of the various metals. The Haloid salts however, when decomposed, yield products similar to the Oxyacid salts. For instance, if Iodide of Potassium be dissolved in water, and dilute Sulphuric Acid added, this acid, being powerful in its chemical affinities, tends to appropriate to itself the alkali; it does not however remove *Potassium* and liberate *Iodine*, but takes the *Oxide* of Potassium and sets free *Hydriodic Acid*. In other words, as an atom of water is produced during the *formation* of a Hydracid salt, so are the elements of water separated in the *decomposition* of a Hydracid salt. The reaction of dilute Sulphuric Acid upon Iodide of Potassium may be stated thus :—

Sulphuric Acid *plus* (Iodine Potassium) *plus* (Hydrogen Oxygen)
equals (Sulphuric Acid, Oxygen Potassium) or Sulphate of Potash,
and (Hydrogen Iodine) or Hydriodic Acid.

All metallic salts with Oxygen acids contain the metal in the state of Oxide, although in the name of the salt the word Oxide is omitted; thus Sulphate of Iron is strictly Sulphate of Oxide of Iron, and Nitrate of Silver, Nitrate of Oxide of Silver. The Oxides of the Alkaline and Earthy Metals, being known long before their Elementary Metals were discovered, have each a name more familiar than that of the metals, hence in the salts with Oxygen acids the former name is employed rather than the latter; thus Nitrate of *Lime* is spoken of, rather than Nitrate of *Oxide of Calcium*. In the haloid salts of these elements, the name of the metal is necessarily made use of; thus Hydrochloric Acid and *Lime* form Chloride of *Calcium* (and water).

Since Acids do not combine with Metals, but only with their Oxides, every metal when dissolving in an

acid obtains Oxygen, either from the water or from the acid, or, in the case of Hydracids, displaces the Hydrogen of the acid, and combines with the remaining element of the acid. Thus, when Zinc or Iron dissolves in dilute Sulphuric Acid, water is decomposed, the Oxygen combining with the metals to form oxides, which unite with the acid, and the other element of the water, Hydrogen, escapes with effervescence. When the same metals dissolve in a Hydrogen acid, as Hydrochloric, Hydrogen is evolved from the acid, and the remaining element, Chlorine, forms with the Zinc or Iron, Chloride of Zinc or Iron. On the other hand, when Silver dissolves in Nitric Acid, the Oxygen required to form Oxide of Silver is derived from the acid, which is thus reduced to a lower Oxide of Nitrogen, which escapes with effervescence.

LAWS OF COMBINATION BY WEIGHT.

These are four in number, and they are of much importance.

1. *Law of Definite Proportion.*—"Every Chemical compound has a perfectly definite composition, and the same compound, from whatever source derived, always has the same elements in the same proportions."

2. *Law of Multiple Proportions.*—"If one body can combine with another in more than one proportion, the other proportions are either double, treble, etc., of the first, or bear some nearly equally simple proportions."

3. *Law of Equivalent Proportions.*—"If certain bodies, as A, B, and C, unite each separately with another, X, the proportions in which they combine with X to form their simplest compounds, are the same (or some simple proportion of the same) in which they combine with each other to form their simplest compounds."

4. *Law of Combining Numbers of Compounds.*—The combining number, or atomic weight, of a compound is the sum of the combining numbers of its constituents.

ATOMIC THEORY.

The remarkable facts stated in these laws have led to a conjecture or theory, termed the Atomic Theory, that however minutely divisible matter may be, it is not *practically infinitely* divisible, but that it consists of ultimate particles which *never are* divided in all the changes which matter undergoes, and which are therefore termed *atoms*, from ἄτομος (uncut). It is supposed that the simplest combination of two elements consist of 1 atom of one united to 1 atom of the other, and as the numbers attached to the elements represent the proportions of the simplest combinations, they also represent the proportional weights of the atoms of each of the elements, or their atomic weights.

In describing the composition of a substance, it is common to speak of it as consisting of *one* atom of one element combined with one atom (or more) of another element, whatever the quantity of the substance may be, meaning that the minutest particle or *atom* of it has this composition.

Practical Application of the Laws of Combination.—The utility of being acquainted with the law of combining proportions is obvious when their nature is understood. As bodies both unite with and replace each other in equivalents, a simple calculation shows at once how much of each element or compound will be required in a given reaction. Thus, supposing it is desired to convert 100 grains of Nitrate of Silver into *Chloride* of Silver, the weight of Chloride of Sodium which will be necessary is deduced thus:—one equivalent, or 170 parts, of Nitrate of Silver is decomposed by an equivalent, or 58·5 parts, of Chloride of Sodium. Therefore, as 170 : 58·5 :: 100 : 34·4; that is, 34·4 grains of salt will precipitate, in the state of Chloride, the whole of the Silver contained in 100 grains of Nitrate.

So again, in order to form the Iodide of Silver, what are the proportions in which the two salts should be

mixed? The equivalent of Iodide of Potassium is 166, and that of Nitrate of Silver is 170. These numbers so nearly correspond, that it is common to direct that *equal weights* of the two salts should be taken.

One more illustration will suffice. Supposing it be required to form 20 *grains* of Iodide of Silver, how much Iodide of Potassium and Nitrate of Silver must be used? One equivalent, or 166 parts, of Iodide of Potassium, will yield an equivalent, or 235 parts, of Iodide of Silver; therefore as 235 : 166 :: 20 : 14·1. Hence, if 14·1 grains of the Iodide of Potassium be dissolved in water, and an equivalent quantity—viz., 14·5 grains—of the Nitrate of Silver added, the yellow precipitate, when washed and dried, will weigh precisely 20 grains.

NOMENCLATURE OF COMPOUNDS.

Compounds of two Elements.—A compound of two elements is distinguished by the name of the first terminating in *-ide*; thus FeO = Ox*ide* of Iron, NaCl = Chlor*ide* of Sodium, KI = Iod*ide* of Potassium. The same termination is also used with compound bodies which possess neither basic nor acid characters when they unite with each other or with an element; thus Cyanogen, CN, a compound neither acid nor basic, unites with Potassium, forming Cyanide of Potassium, K,CN or KCy. So also the salts produced by the combination of Hydrogen acids with bases, since they are compounds of only two elements, in consequence of the separation of Hydrogen and Oxygen as water, are named in the same way. Salts of this kind may be produced either by the union of two elements, or by the union of an acid and base.

$$KHO + HI = KI + H_2O.$$
$$NaHO + HCl = NaCl + H_2O.$$
$$KHO + HCy = KCy + H_2O.$$

The combinations of Sulphur, Carbon, and Phosphorus with other elements used to be distinguished by the

termination *-uret*, as FeS = Sulph*uret* of Iron, but the termination *-ide* is now generally used with all *binary* compounds, or compounds of two elements. Phosphide, or Sulphide, or Carbide of Iron, are now the terms used instead of Phosphuret, Sulphuret, and Carburet of Iron.

When one element combines with another in more than one proportion, it was, under the old system of nomenclature, customary to distinguish the compound which consists of an atom of each by the prefix *proto-*, as $FeCl_2$ = *Proto*chloride of Iron, N_2O = *Proto*xide of Nitrogen; the compound of 3 atoms of the first-named* with two atoms of the second element has the prefix *sesqui-*, as Fe_2Cl_6 = *Sesqui*chloride of Iron; the prefix *bi-* or *bin-* signifies 2 atoms of the first to 1 of the second, and *per-*, the compound, *not acid*, which contains the *largest* amount of the same element; thus, MnO_2 is the Binoxide and also the Peroxide of Manganese, as it is the highest non-acid oxide of that metal.

Compounds which contained more than one atom of the *second-named* element to one of the first, were classified as *sub*-compounds; the *quantity* being defined by other prefixes, as *di-* and *tri-*, which were the reverse of *bi-* and *ter-*, and signifying one atom of the first-named to two and three respectively of the other element.

Under the new system the Greek prefixes *mono-*, *di-*, *tri-*, *tetra-*, &c., alone are employed to distinguish between the different compounds. Thus, Silver Monoxide (Ag_2O) represents the combination between silver and the lowest quantity of oxygen.

Acids and Salts.—If but one acid is known as resulting from the union of two elements, its name ends in *ic*; this is always the case with the Hydrogen acids. In the case of Oxygen acids, when there is a series of acids produced by the combination of an element with Oxygen, that which contains the largest amount of Oxygen terminates in *-ic*, the next which contains less

* *First* and *second* relates to the order of the elements in the *names* of the compounds, and not to their order in the formulæ.

ends in *-ous*, and if there be a third with still less the prefix *hypo-* is used: thus, bearing in mind what has been previously said, HNO_3 = Nitr*ic* Acid, HNO_2 = Nitr*ous* Acid; H_2SO_4 = Sulphur*ic* Acid, H_2SO_3 = Sulphur*ous* Acid, and H_2SO_2 = *Hypo*sulphur*ous* Acid.

Sometimes after distinguishing the highest known acid of a series with the termination *-ic*, another acid is discovered with still more Oxygen, in this case the new compound has the prefix *per-* attached: thus, after $HClO_3$ = Chloric Acid was named, another acid, $HClO_4$, was discovered, and named *Per*chloric Acid.

In the name of a salt the *-ic* of the acid is changed into *-ate*, and *-ous* into *-ite*; thus, Sulphur*ic* Acid forms Sulph*ates*, and Sulphur*ous* Acid forms Sulph*ites*; the prefixes of the acids, as *Hypo-* or *Per-*, being retained in the salt, as *Hypo*sulphite of Soda, *Per*manganate of Potash.

A chemically neutral salt is one which has as many atoms of acid as there are atoms of Oxygen in the base, thus Fe,SO_4 and $Fe_2O_3,3SO_3$ are each *chemically* neutral (though from the weakness of their bases, quite acid to test-paper); such salts were most correctly distinguished as Sulphate of the Protoxide, and Sulphate of the Sesquioxide of Iron, the name of the oxide indicating the number of atoms of acid they must contain; commonly, however, the prefix which distinguishes the oxide is transferred to the acid, and the above-named salts are thus called *Proto*sulphate and *Sesqui*sulphate of Iron. But these and similar salts are now more commonly described as Ferrous Sulphate and Ferric Sulphate, or in other words as Sulphates respectively of the Ferrous and Ferric Oxides. Prefixes to the acid in a salt ought properly to be confined to those cases in which there are not the same number of atoms of acid as there are of Oxygen in the base, the prefixes sesqui-, bi-, ter-, di-, and tri- having the same meanings as in the case of compounds of two elements, the three first being applied to *chemically* acid, and the two latter to a *chemically* basic salts.

In salts derived from Hydrogen acids, since they are binary compounds, the prefix of the oxide is necessarily transferred to the *residue* of the acid; thus Hydrochloric Acid forms with *Sesquioxide* of Iron, *Sesquichloride* of Iron (and water). $Fe_2O_3 + 6HCl = Fe_2Cl_6 + 3H_2O$.

CHEMICAL CHANGES.

Chemical changes, whether they be the result of combination or of decomposition, or of interchange of elements between compounds, are often attended with striking phenomena, such as the evolution of light and heat, or with remarkable alterations of condition, as from gas to liquid, or from liquid to solid, etc.; but the changes most familiar to the Photographer and the Analyst are those of colour and of solubility. With regard to the latter, it is well here to explain one or two terms. A body is said to *dissolve* in a liquid, when it disappears in the liquid, leaving the latter *transparent*, even though it may be coloured. Two transparent solutions, when mixed, often produce a *precipitate*, a term which is applied to *insoluble* matter suddenly appearing in a liquid previously clear, and rendering it opaque and turbid.

Precipitates can be separated either by *Decantation* or *Filtration*. The first method, Decantation, is allowing the precipitate to fall by its own weight to the bottom of the liquid, and then pouring the latter off. Filtration is effected by pouring the whole liquid and precipitate on a piece of porous paper, folded into a conical form, termed a *Filter*, and supported in a *Funnel*; the liquid passes through the paper in a transparent state, and the *precipitate* remains upon it. But chemical changes are here referred to chiefly for the purpose of pointing out the varieties of *internal* change which bodies may undergo when brought into contact with each other; these internal changes manifesting themselves often in the *visible* phenomena above alluded to.

Alterations of composition may usually be referred to one of the following heads :—

1. Simple and direct union of two elements.—Thus, Sulphur combines with the Oxygen of the atmosphere when heated to a certain point, the union being known as "burning," and the product is Sulphurous Acid, H_2SO_3. The element Iron "rusts" by combining with Oxygen.

2. Union of compounds with elements.—Thus, Sulphurous Acid, H_2SO_3, by exposure to air can combine with more Oxygen. $H_2SO_3 + O = H_2SO_4$ = Sulphuric Acid. Protoxide of Iron, FeO, by exposure to air becomes Fe_2O_3.

$$2FeO + O = Fe_2O_3.$$

3. Union of compounds with each other, as in the formation of salts with Oxygen Acids.

$$KHO + HSO_4 = KSO_4 + H_2O = \text{Sulphate of Potash.}$$

Two salts sometimes unite together to form a double salt. Alum is an example, it is a double salt of Sulphate of Alumina and Sulphate of Potash.

The double Chloride of Gold and Sodium is another example, $AuCl_3 + NaCl + 4HO$.

4. Displacement, or single decomposition, is where one element or compound displaces another element or compound from its state of combination.

Thus Chlorine acting on Iodide of Potassium, immediately takes the Potassium, and sets Iodine free, a change which is rendered evident from the black colour of the Iodine. $KI + Cl = KCl + I$.

One metal often *precipitates* another from its solution by displacing it; thus Zinc placed in a solution of Acetate of Lead combines with the Acetic Acid and Oxygen of the Oxide of Lead, and is dissolved, while the latter is thrown down in an arborescent form, known as the "Lead tree."

A piece of metallic Copper, placed in a solution of

Nitrate of Silver, will speedily throw down metallic Silver, and form Nitrate of Copper.

One Oxide is often used to separate another Oxide; thus Oxide of Silver is obtained by adding a solution of Potash to a solution of Nitrate of Silver.

$$2AgNO_3 + 2KHO = Ag_2O + 2KNO_3 + H_2O.$$

5. Double decomposition is the mutual interchange of the atoms of two compounds; in the case of solutions, this is often attended with precipitation; thus, in the preparation of Nitrate of Iron from Nitrate of Baryta and Sulphate of Iron, there is a mutual interchange, resulting in Nitrate of Iron and Sulphate of Baryta, which is precipitated.

In the sensitizing of Salted Paper with Nitrate of Silver, Chloride of Silver is precipitated in the Paper, the change being $Ag,NO_3 + NaCl = Na,NO_3 + AgCl$.

6. Substitution.—This is only a variety of displacement or of double decomposition, but the term is used chiefly in cases where one of the compounds that has undergone the displacement, is little, if at all, altered in appearance, as in the case of Cotton transformed into Gun-cotton. Here a certain number of atoms of Hydrogen have been displaced by Peroxide of Nitrogen, but the appearance of the Cotton is little, if at all, changed.

7. Decomposition, into simpler compounds or elements, as of Chloride of Silver by light, which resolves it into Subchloride (?) of Silver and Chlorine; strong Nitric Acid by light is decomposed into NO_2 and O. Chlorate and Iodate of Potash by heat are resolved into Oxygen, and Chloride and Iodide of Potassium.

$$K,ClO_3 = KCl + O_3.$$
$$K,IO_3 = KI + O_3.$$

Several of the compounds of Gold, Silver, Platinum, and Mercury are entirely decomposed into their elements by heat.

ON THE CHEMISTRY OF ORGANIC SUBSTANCES.

The term organic is applied to substances produced either by vegetables or animals, or which are obtained by chemical processes from them; thus Wood, and Acetic Acid procured by its distillation, and Sugar, with the Alcohol derived from it by fermentation, are organic substances.

All organic bodies are compounds of Carbon, and the class embraces a great variety of products, which, like inorganic bodies, include neutral, acid, basic, and saline compounds.

The organic *acids* are numerous, such as Acetic Acid, Tartaric, Citric, and a variety of others.

The *neutral substances* cannot easily be assimilated to any class of inorganic compounds; as examples, take Starch, Sugar, Lignine, etc.

The *bases* are also a large class. Morphia, obtained from Opium; Quinia, from Quinine; Nicotine, from Tobacco, are illustrations.

Besides these, there are large classes of compounds known as Alcohols, Ethers, Aldehyds, etc., to which there is nothing analogous in inorganic chemistry.

Alcohols are Carbon compounds, which by union with acids form neutral bodies, termed Ether, Water being separated.

Ethers are either Alcohol, ÷ Acid *minus* Water, or 2 Alcohol *minus* 2 Water.

Aldehyds are Alcohols *minus* Hydrogen, and by the absorption of Oxygen they form Acids.

Composition of Organic and Inorganic Bodies Contrasted.—There are more than fifty elementary substances found in the inorganic kingdom, but only *four*, commonly speaking, in the organic: these four are Carbon, Hydrogen, Nitrogen, and Oxygen.

Some organic bodies—oil of turpentine, naphtha, etc. —contain only Carbon and Hydrogen; many others, such as sugar, gum, alcohols, fats, vegetable acids,—Carbon, Hydrogen, and Oxygen. The *Nitrogenous bodies*, so

called, contain Nitrogen in addition to the other elements: such are Albumen, Caseine, Gelatine, and all natural organic bases; Sulphur and Phosphorus are also present in many of the Nitrogenous bodies, but only to a small extent.

Organic substances, although simple as regards the *number* of elements involved in their formation, are often highly complex in the arrangement of the atoms; this may be illustrated by the following formulæ:—

Starch	$C_6H_{10}O_5$.
Cane Sugar	$C_{12}H_{22}O_{11}$.
Grape Sugar	$C_6H_{12}O_6$.

Inorganic bodies, as already shown, unite *in pairs*—two elements join to form a binary compound; two binary compounds produce a salt; two salts associated together form a double salt. With organic bodies however the arrangement is often different—the elementary atoms are all grouped equally in one compound atom, which is highly complex in structure, and cannot be split up into binary products.

Observe also, as characteristic of Organic Chemistry, the apparent similarity in composition between bodies which differ widely in properties. As examples take *Lignine*, or cotton fibre, and *Starch*—each of which contains the same percentage of Carbon, Hydrogen, and Oxygen.

Mode of Distinguishing between Organic and Inorganic Matter.—A simple means of doing this is as follows:—place the suspected substance upon a piece of Platinum-foil, and heat it to redness with a spirit-lamp: if it first *blackens*, and then burns completely away, it is probably of organic origin. This test depends upon the fact, that all organic bodies contain Carbon, and that their other constituent elements are either themselves volatile, or capable of forming volatile combinations with Oxygen. Inorganic substances, on the other hand, are often unaffected by heat, or, if volatile, are dissipated without previous charring.

The action of heat upon organic matter may be illustrated by the combustion of coal or wood in an ordinary furnace:—first, an escape of Carbon and Hydrogen, united in the form of volatile gaseous matter, takes place, leaving behind a black cinder, which consists of Carbon and inorganic matter combined; afterwards this Carbon burns away into Carbonic Acid, and a grey ash is left, which is composed of inorganic salts, and is indestructible by heat.

This test is of course not applicable to organic bodies volatile without decomposition, as Alcohol, Ether, Camphor, etc.; but these also are generally not the varieties of organic matter which trouble the Photographer.

CHAPTER II.

VOCABULARY OF PHOTOGRAPHIC CHEMICALS.*

ACETIC ACID.

Formula of Glacial Acid, $HC_2H_3O_2$.

Acetic Acid is a product of the *oxidation* of Alcohol, C_2H_6O. Alcohol, when perfectly pure, is not affected by exposure to air; but if it be diluted, and a portion of yeast be added, it soon acts as a *ferment*, and causes the spirit to unite with Ogygen derived from the atmosphere, and so to become *sour* from formation of Acetic Acid, or "vinegar."

Acetic Acid is also produced on a large scale by heating *wood* in close vessels: a substance distils over which is Acetic Acid contaminated with empyreumatic and tarry matter; it is termed Pyroligneous Acid, and is much used in commerce.

The most concentrated Acetic Acid may be obtained by neutralizing common vinegar with Carbonate of Soda, and crystallizing out the Acetate of Soda so formed; the Acetate must then be deprived of its water of crystallization, and fused at a gentle heat. After cooling, 82 parts of the salt are to be distilled with 98 of strong Sulphuric Acid, which removes the Soda and liberates Acetic Acid: the Acetic Acid, being volatile, distils over, and may be condensed.

Properties of Acetic Acid.—The strongest acid contains only a single atom of water; it is sold under

* N.B. The arrangement in this Vocabulary is made with reference to the second constituent in compounds. Thus, *Acetic Ether* will be found under the head of "Ether, Acetic," *Nitrate of Silver* as "Silver, Nitrate of," *Iodide of Potassium* as "Potassium, Iodide of," etc. *Acids* will be found under their special names.

the name of "Glacial Acetic Acid," so called from its property of solidifying at a moderately low temperature. At about 50° the crystals melt, and form a limpid liquid of pungent odour and a density nearly corresponding to that of water; the specific gravity of Acetic Acid however is no test of its real strength, which can only be estimated by analysis.

The commercial *Glacial* Acetic Acid, so termed, is usually diluted with water, and sometimes a trace of Sulphurous Acid is introduced, as the Writer is informed, to confer the property of solidifying in cold weather, and thus to give an appearance of strength. It is however probably due in most cases to the decomposition of the Sulphuric Acid used to obtain it. Sulphurous and Hydrochloric Acids are both injurious in Photographic Processes, from their property of precipitating Nitrate of Silver. To detect them, proceed as follows:—Dissolve a small crystal of Nitrate of Silver in a few drops of water, and add to it about half a drachm of the Glacial Acid; the mixture should remain quite clear even when exposed to light. Hydrochloric and Sulphurous Acid produce a white deposit of Chloride or Sulphite of Silver, distinguishable by Nitric Acid, which dissolves the Sulphite, but leaves the Chloride unchanged; and if *Aldehyde* or volatile tarry matter be present in the Acetic Acid, the mixture with Nitrate of Silver, although clear at first, becomes discoloured by the action of light.

Glacial Acetic Acid sometimes has a smell of garlic. In this case it probably contains an organic Sulphur Acid, and is unfit for use.

Many employ a cheaper form of Acetic Acid, sold by druggists as "Beaufoy's" acid; it should be of the strength of the Acetic Acid Fortiss. of the London Pharmacopœia, containing 30 per cent. real acid. It will be advisable to test it for Sulphuric Acid, and other impurities, before use. When a certain quantity of the Glacial Acid is advised in a formula, take three times as much of the Beaufoy's Acid.

ALBUMEN.

Albumen is an organic principle found both in the animal and vegetable kingdom. Its properties are best studied in the *white of egg*, which is a very pure form of Albumen.

Albumen is capable of existing in two states; in one of which it is soluble, in the other insoluble, in water. The aqueous solution of the soluble variety gives a slightly alkaline reaction to test-paper; it is somewhat thick and glutinous, but becomes more fluid on the addition of a small quantity of an alkali, such as Potash or Ammonia.

Soluble Albumen may be converted into the *insoluble* form in the following ways:—

1. *By the application of heat.*—A moderately strong solution of Albumen becomes opalescent and coagulates on being heated to about 150° Fahrenheit, but a temperature of 212° is required if the liquid is very dilute. A layer of *dried* Albumen is not rendered insoluble by *dry* heat of 212°.

2. *By addition of strong acids.*—Nitric Acid coagulates Albumen perfectly without the aid of heat. Acetic Acid however acts differently, appearing to enter into combination with the Albumen, and forming a compound soluble in warm water acidified by Acetic Acid.

3. *By the action of metallic salts.*—Many of the salts of the metals coagulate Albumen completely. Nitrate of Silver does so; also the Bichloride of Mercury. Ammonio-Nitrate of Silver however does not coagulate Albumen.

The white precipitate formed on mixing Albumen with Nitrate of Silver is a chemical compound of the animal matter with Protoxide of Silver, and has been termed Albuminate of Silver: its properties will be described afterwards. On heating in a current of Hydrogen gas, it assumes a brick-red colour, being probably reduced to the condition of a compound with *Suboxide* of Silver. It is then almost insoluble in

Ammonia, but enough dissolves to tinge the liquid wine-red. The *red coloration* of solution of Nitrate of Silver employed in sensitizing the Albuminized Photographic paper is doubtless produced by the same compound, although often referred to the presence of Sulphide of Silver.

Albumen also combines with Lime and Baryta. When Chloride of Barium is used with Albumen, a white precipitate of this kind usually forms.

By long keeping, Albumen loses its alkaline reaction and becomes sour and more limpid than at first. Mucous threads like cobwebs form in it, which appear to be caused by oxidation. Ammonia added to Albumen is said to preserve it for a longer time, and a lump of camphor floated in the liquid has also a good effect. Decomposed Albumen usually contains Sulphuretted Hydrogen.

Chemical composition of Albumen.—The following is the composition of Albumen according to Lieberkühn :—

Carbon	53·3
Hydrogen	7·1
Nitrogen	15·7
Oxygen	22·1
Sulphur	1·8
	100·0

ALCOHOL.

Formula, C_2H_6O.

Alcohol is obtained by the careful distillation of any spirituous or fermented liquor. If wine or beer be placed in a retort, and heat applied, the Alcohol, being more volatile than water, rises first, and may be condensed in an appropriate receiver; a portion of the vapour of water however passes over with the Alcohol, and dilutes it to a certain extent, forming what is

termed "Spirit of Wine." Much of this water may be removed by redistillation from Carbonate of Potash; but in order to render the Alcohol thoroughly *anhydrous*, it is necessary to employ *quicklime*, which possesses a still greater attraction for water. For this purpose strong Alcohol of ·823 should be left in contact with powdered quicklime for three or four days, or until the latter has ceased to swell from absorption of water, after which it is separated by distillation, the retort being placed in a water-bath.

Properties of Alcohol.—Pure anhydrous or absolute Alcohol is a limpid liquid, of an agreeable odour and pungent taste; sp. gr. at 60°, ·794. It absorbs vapour of water, and becomes diluted by exposure to damp air; boils at 173° Fahr. It has never been frozen.

Alcohol distilled from Carbonate of Potash has a specific gravity of ·815 to ·823, and contains 90 to 93 per cent. of real spirit.

The specific gravity of ordinary rectified Spirits of Wine is about ·836, and it contains 80 to 83 per cent. of absolute Alcohol.

Different Commercial Qualities of Alcohol.—Alcohol really absolute is not often used in Photography; the expense of making it is very great, and it could not be prepared at a profit. A Spirit with less than four per cent. of water (sp. gr. ·805) may be obtained by agitating commercial Spirit of Wine first with Carbonate of Potash in the manner presently to be advised, and then with a common quality of dry Chloride of Calcium. Put in about three-quarters of a pound of the Chloride of Calcium to half a gallon of Spirit of ·815; the greater part dissolves with perceptible rise of temperature. Draw over as much as possible in a steam bath; and, to prevent the residue in the retort from setting into a hard mass, it is well to add a little water to it, after the distillation is completed. In this way the commercial absolute Alcohol is usually prepared.

The next quality of Spirit is the strong Alcohol of ·815 to ·823. This may be obtained by agitating

Spirit of Wine, ·836, with an excess of dry Carbonate of Potash. The salt termed Carbonate of Potash is a *deliquescent* salt, having a great attraction for water; consequently, when Spirit of Wine is shaken with Carbonate of Potash, a portion of water is removed, the salt dissolving in it and forming a dense liquid, which refuses to mix with the Alcohol, and sinks to the bottom. At the expiration of two or three days, if the bottle has been shaken frequently, the action is complete, and the lower stratum of fluid may be drawn off and rejected.

In order to obtain the greatest amount of concentration, it will be necessary to have a series of vessels, each containing about a pound of the Carbonate to a gallon of Spirit. The Alcohol may be passed from one to the other, and should not be distilled until the finely-powdered Carbonate can be shaken about in the liquid without being wetted. The Carbonate which the Writer employs is nearly pure, and costs from a shilling to eighteen-pence per pound; it must be dried on a hot metal plate before use. A commoner variety would answer, but it has the disadvantage of clotting together at the bottom of the vessel, and of not dissolving into a clear liquid.

A third quality of commercial Alcohol is the rectified Spirit of Wine of ·836 already referred to; it is very suitable for adding to developing fluids, etc., but not sufficiently strong for good Collodion.

Alcohol for Collodion Photography.—For a long time the Writer was in the habit of employing rectified Spirit of Wine for the preparation of Collodion, increasing its strength as far as necessary, by means of dry Carbonate of Potash; but having at length become dissatisfied with the smell of certain samples of this rectified Spirit, he has since used a strong Alcohol obtained by one distillation. In rectifying Spirit, a liquid known as "faints" is sometimes mixed with the purer Spirit for the sake of economy, and these faints are invariably contaminated with essential Oils. It is

most important in Photography to avoid essential Oils, and therefore the grain Spirit obtained by one distillation in a Coffey's still may be preferred. In taking the specific gravity of this grain Spirit, which varies from ·817 to ·819 at 60° Fahr., we see at once the advantage likely to accrue from its employment, since the Fusel Oil, which boils at a more elevated temperature, cannot rise so high in the still, and is separated. The smell of the grain Spirit is very sweet; and although it is not quite so strong as is required, yet by converting a portion of it into Alcohol of ·805, by means of dry Chloride of Calcium, and mixing this with the remainder, the correct specific gravity may easily be obtained.

The reaction to test-paper of the pure grain Spirit should be quite neutral; but in some instances a trace of acid is present, so that each half-gallon of Spirit requires about one drop of solution of Ammonia of sp. gr. 0·93. The Writer has never yet found in this or in any other spirit the alkaline reaction which is exhibited by Ether.

ALCOHOL (*Methylated*).

Spirit of Wine containing ten per cent. of Wood Naphtha is allowed by the excise laws to be sold free of duty, under the name of "Methylated Spirit." The quality, however, is often inferior, since residues containing Fusel Oil and other volatile bodies are usually rectified for the purpose of methylating.

ALCOHOL, METHYLIC (*Wood Naphtha—Pyroxylic Spirit.*)

Formula, CH_4O.

This liquid is one of the products of the destructive distillation of wood, and constitutes a large portion of the inflammable fluid called Wood Naphtha, or Pyr-

oxylic Spirit. In its pure state it much resembles common Alcohol in its properties. As common Alcohol by oxidation furnishes an Acid, the Acetic, so Methylic Alcohol in like manner yields a similar Acid, called Formic Acid.

ALUM.

Formula, $AlK(SO_4)_2 + 12H_2O = 474{\cdot}5$.

The common Alum of commerce, or Potash Alum, is found native in some places, but is also manufactured on an extensive scale. It is soluble in 18 parts of cold water and in rather less than its own weight of boiling water. It tastes astringent and acidulous, is styptic, reddens litmus, and loses its water of crystallization by being heated.

Its use in Photography is mainly confined to imparting hardness and insolubility to gelatine films on either glass or paper, for which purpose Chrome Alum is also employed. When mixed with Citric or other similar acids it serves a useful purpose in clearing gelatine negatives that have become discoloured by the developer.

Much of the common Alum contains Ammonia as well as Potassium.

AMMONIA.

Formula, $NH_3 = 17$.

The liquid known by this name is an aqueous solution of the volatile gas Ammonia. Ammoniacal gas contains one atom of Nitrogen combined with three of Hydrogen: these two elementary bodies, when free, show no tendency to combine, but they can be made to unite under certain circumstances, and the result is Ammonia.

Properties of Ammonia.—Ammoniacal gas is soluble in water to a large extent: the solution possessing those properties which are termed alkaline. Ammonia, how-

ever, differs from the other alkalies in one important particular—it is volatile: hence the original colour of turmeric-paper affected by Ammonia is restored on the application of heat. Solution of Ammonia absorbs Carbonic Acid rapidly from the air, and is converted into Carbonate of Ammonia; it should therefore be preserved in stoppered bottles. Besides Carbonate, commercial Ammonia often contains Chloride of Ammonium, recognized by the white precipitate given by Nitrate of Silver after acidifying with pure Nitric Acid.

The strength of commercial Ammonia varies greatly; that sold for pharmaceutical purposes under the name of Liquor Ammoniæ contains about ten per cent. of real Ammonia. The sp. gr. of aqueous Ammonia *diminishes* with the portion of Ammonia present, the Liquor Ammoniæ being usually about ·936. It is a common error in Photographic operations to confound the diluted Ammonia with the Liquor Ammoniæ Fort., which is so strong that a single drop will neutralize a large portion of acid, and has sp. gr. of only ·88.

Ammonia has no resemblance in composition to other bases which are metallic oxides, and it differs from them also, in that it never combines with Oxygen acids without including water as an essential ingredient in the compound. Yet the salts of Ammonia have a close resemblance in properties to those of the alkalies Potash and Soda, and this resemblance has led to the *Ammonium Theory*, which develops a close resemblance *in composition* between the salts of Ammonia and of the alkalies, and also explains why water is *essential* to the salts with Oxygen acids.

AMMONIA, BICHROMATE OF.

Formula, $NH_4Cr_2O_7 = 234{\cdot}4$.

This salt is obtained by dividing a solution of Chromic Acid into two parts, neutralizing one with Ammonia, then adding the other part and evaporating.

The resulting crystals are permanent and soluble in water.

Bichromate of Ammonia is used in many Photographic processes, dependent on the peculiar property of this salt in rendering certain organic bodies, such as Albumen, Gelatine, etc., insoluble in their usual menstrua, after exposure to light.

The rationale of the various processes seems to be this. The Bichromate, in contact with the Gelatine or other organic body and exposed to Light, gives up part of its Oxygen to the organic body, which is thus rendered insoluble in warm water in exact proportion to the extent of the Actinic action.

AMMONIA, CARBONATE OF.

This occurs commercially in lumps of a considerable size, obtained by sublimation. Its composition is rather variable. When first formed it has nearly the composition of a Sesquicarbonate, but by exposure to the air neutral Carbonate of Ammonia escapes, and a white powder is left, which is a Bicarbonate.

AMMONIUM SULPHIDE (or Sulphydrate).

Formula, $NH_4,HS = 51$.

This solution is formed by passing Sulphuretted Hydrogen through Ammonia. It is used in Photography for precipitating silver solutions, and for intensifying Negatives. The latter object it accomplishes by changing the deposit on the developed image into a dense black colour which obstructs the Actinic rays.

The solution should be kept in a well-stoppered bottle, and at a distance from the dark room, because the fumes given off are exceedingly prejudicial to other operations which have to be performed there.

AMMONIA, NITRATE OF.

Formula, $NH_4NO_3 = 80$.

This is a neutral combination of Nitric Acid and Ammonia, which may be crystallized without difficulty. It is gradually formed in the Photographic Nitrate Bath when compounds of Ammonium are used in iodizing.

Nitrate of Ammonia is not of itself alkaline, but inasmuch as it is a solvent of Oxide and also of Carbonate of Silver, a Bath containing Nitrate of Ammonia will give a strong Alkaline reaction on adding to it either Potash, Ammonia, or Chalk.

When heated, Nitrous Oxide, or Laughing Gas, is evolved. Its solution in water is attended by an intense degree of cold.

AMMONIUM, BROMIDE OF.

Formula, $NH_4Br = 98$.

This is a crystalized salt, which may be prepared by precipitating Bromide of Calcium by Carbonate of Ammonia. It is very soluble in water, and is more easily dissolved by Alcohol and Ether than the corresponding Bromide of Potassium. It does not become coloured on keeping, like the Iodide of Ammonium.

Bromide of Ammonium is a better form of Bromide for Collodion than the corresponding Salt of Potassium or Cadmium, and it can usually be obtained in a pure state.

AMMONIUM, CHLORIDE OF.

Formula, $NH_4Cl = 53{\cdot}5$.

This salt, also known as Muriate or Hydrochlorate of Ammonia, occurs in commerce in the form of colourless and translucent masses, which are procured by *sublimation*, the dry salt being volatile when strongly

heated. It dissolves in an equal weight of boiling, or in three parts of cold water. It contains more Chlorine in proportion to the weight used than Chloride of Sodium, the atomic weights of the two being as 53·5 to 58·5.

Chloride of Ammonium is easily obtained in a pure state, and is, on the whole, more suitable for salting paper than either Chloride of Sodium or Chloride of Barium.

AMMONIUM, IODIDE OF,

Formula, $NH_4I = 145$,

Is a salt very valuable in Collodion, because it has the property of conferring limpidity, sensitiveness, and adherency to the glass, which other Iodides do not always possess. It is, however, an unstable substance, prone to liberate Iodine and to decompose the Collodion in which it is dissolved, unless this bad effect is neutralized by Iodide of Cadmium, which has an opposite tendency.

To decolorize Iodide of Ammonium which has been decomposed by keeping, shake it up with a little strong Ether; the Iodine will be dissolved out, and, unless Alcohol be present, no great loss from solution will result.

AMMONIUM, SULPHOCYANIDE OF.

(*See* SULPHOCYANIDES.)

ANILINE.

Formula, $C_6H_7N = 93$.

This powerful base is derived from Indigo, Nitrobenzol, Coal-tar, etc.

When pure, Aniline is a thin, colourless, and highly refracting oil, of a burning taste and aromatic flavour.

With acids it forms a remarkable series of salts, which crystallize with great beauty and facility.

With Chromic Acid it gives a deep green or bluish-black colour, which has been taken advantage of by Mr. Willis in his Photographic process for copying drawings.

AQUA REGIA. (*See* NITRO-HYDROCHLORIC ACID.)

ARSENIC, BROMIDE OF.

Formula, $AsBr_3 = 315$.

Bromide of Arsenic has been used in Collodion for the purpose of increasing the intensity of the developed image. A solution suitable for that purpose may be prepared by reducing Metallic Arsenic to a fine powder and placing it in a dry bottle with Alcohol of sp. gr. ·805. Bromine is then to be dropped into the Alcohol, when immediate combination will ensue: the Arsenic must always be in excess.

The addition of water decomposes Bromide of Arsenic into Arsenious Acid and Hydrobromic Acid; hence the necessity for using Alcohol of considerable strength.

AURO-CHLORIDE OF SODIUM.

(*See* SODIUM, AURO-CHLORIDE OF.)

BARIUM, CHLORIDE OF.

Formula, $BaCl_2 + 2\,Aq. = 244$.

Barium is a metallic element very closely allied to Calcium, the elementary basis of *Lime*. The Chloride of Barium is commonly employed as a test for Sulphuric Acid, with which it forms an insoluble precipi-

tate of Sulphate of Baryta. It also slightly alters the colour of the Photographic image when used in preparing Positive paper, which may be due, in some measure, to a chemical combination of Baryta with Albumen: but it must be remembered that this Chloride, from its high atomic weight, contains *less Chlorine* than the alkaline Chlorides.

Properties of Chloride of Barium.—Chloride of Barium occurs in the form of white crystals, soluble in about two parts of water, at common temperatures. These crystals contain two atoms of water of crystallization, which are expelled at 212°, leaving the anhydrous Chloride.

BARYTA, NITRATE OF.

Formula, $Ba(NO_3)_2 = 261$.

Nitrate of Barium forms octohedral crystals, which are anhydrous. It is considerably less soluble than the Chloride of Barium, requiring for solution twelve parts of cold and four of boiling water. It may be substituted for the Nitrate of Lead in the preparation of Protonitrate of Iron. Its addition to the Negative Nitrate Bath prevents the formation of pin-holes in the Collodion film.

BENZOLE.

Formula, $C_{12}H_6 = 78$.

A limpid liquid, obtained commercially by distilling off the most volatile constituent of the substance known as "Coal Naphtha." It does not mix with water, but is dissolved in any quantity by Alcohol or Ether.

Benzole is an excellent solvent of fats and oils, and may be employed for removing grease-spots. It also dissolves Gutta-percha and Caoutchouc. A rapidly drying varnish may be made with Benzole, but it should first be purified by redistillation, since ordinary Benzole sometimes leaves a greasy residue on drying.

BITUMEN OF JUDÆA, OR ASPHALTUM.

This is an indurated pitch found in the Dead Sea, in Trinidad, and many other places.

It is the basis of most black varnishes, being soluble in Naphtha and some other substances.

Being sensitive to light, it has also been used in several Photographic and Photo-engraving processes.

BROMIDES, TEST FOR PURITY.

The most common impurity in Bromides is an Iodide. This impurity is of little or no consequence in the wet Collodion process, or when sensitizing Bromized Collodion in a Nitrate bath; but it is prejudicial in all the *emulsion* processes, because the particles of Iodide of Silver thus formed are much coarser than the Bromide, falling to the bottom of the Collodion very speedily and carrying with them a proportion of Bromide.

Dissolve four or five grains of the suspected Bromide in an ounce or two of distilled water in a test-tube. In another similar test-tube have distilled water only. Now dip the end of a clean glass rod into a solution of Chloride of Palladium, and with it stir up the Bromide solution. With another rod do the same with the distilled water. If Iodide is absent, both tubes when held up to the light will be equally transparent; but if the least trace of Iodide be mixed with the Bromide a brownish red colour will instantly be struck.

This is a most delicate test for an Iodide, and should never be omitted when one wishes to have his Bromized emulsion of Silver in the finest possible state.

BROMINE.

Symbol, Br = 80.

This elementary substance is obtained from the uncrystallizable residium of sea-water, termed *bittern*.

It exists in the water in very minute proportions, combined with Magnesium in the form of a soluble Bromide of Magnesium.

Properties.—Bromine is a deep reddish brown liquid of a disagreeable odour, which gives off ruddy vapours at common temperatures; sparingly soluble in water (1 part in 23, Löwig), but more abundantly so in Alcohol, and especially in Ether. It is very heavy, having a specific gravity of 3·0.

Bromine is closely analogous to Chlorine and Iodine in its chemical properties. It stands intermediately between the two; its affinities being stronger than those of Iodine, but weaker than Chlorine.

It forms a large class of salts, of which the Bromides of Potassium, Ammonium, Cadmium, and Silver are the most familiar to Photographers.

CADMIUM.

Symbol, Cd = 56.

A white metal, resembling Tin in its physical properties. Its Oxide is found associated with Zinc in certain of the ores of the latter, but the two are easily separated.

The Iodide and Bromide of Cadmium are used in Photography, on account of their permanency, and the facility with which they dissolve in Ether and Alcohol.

Metallic Cadmium is sometimes employed to remove free Iodine from Collodion.

CADMIUM, BROMIDE OF.

Formula, $Cd,Br_2 + 4H_2O = 344$.

This salt is much used in Photography, on account of its great stability, and its solubility in Collodion.

It is prepared by heating an excess of the filings of the metal Cadmium with Hydro bromic Acid and water. By evaporation acicular crystals are formed, which constitute the Bromide of commerce, and contain four

equivalents of water of crystallization. This water is expelled by heating the Bromide in a porcelain evaporating dish on a sand-bath placed over a Bunsen's gas-burner. After a time the Bromide melts into a pasty mass in its own water of crystallization, and at last solidifies into a hard cake. It is better, however, when the Bromide is in the pasty state to keep stirring it occasionally with a glass rod, to promote the complete expulsion of the water. The product is now pounded up and kept in a stock bottle.

If the heat is raised too high a risk is run of the Bromide decomposing, the symptoms of which is the liberation of Bromine, most easily detected by the sense of smell. In such case remove the flame or the dish for a short time until the temperature has been brought lower.

CADMIUM, IODIDE OF.

Formula, $CdI_2 = 366$.

This salt is formed by heating filings of metallic Cadmium with Iodine, or by mixing the two with addition of water.

Iodide of Cadmium is very soluble, both in Alcohol and water; the solution yielding on evaporation large six-sided tables of a pearly lustre, which are permanent in the air. The commercial Iodide is sometimes contaminated with Iodide of Zinc, the crystals being imperfectly formed, and slowly liberating Iodine when dissolved in Ether and Alcohol. Pure Iodide of Cadmium remains nearly or quite colourless in Collodion, if the fluid be kept in a cool and dark place.

CALCIUM, BROMIDE OF.

Formula, $CaBr_2 + 4H_2O = 272$.

This salt may be obtained in various ways. The simplest, and perhaps the best, plan is by saturating Hydrobromic Acid with Carbonate of Lime.

Its aqueous solution, when evaporated, yields silky hydrated crystals. It is not much used in Photography.

CALCIUM, CHLORIDE OF.

Formula, $CaCl_2 = 111$.

This salt is found in sea-water; but is usually prepared artificially by dissolving Chalk in Hydrochloric Acid and evaporating. When strongly dried, it occurs in lumps which are hard and difficult to pulverize.

Chloride of Calcium has a great attraction for water, and is used for drying gases and other purposes. Exposed to the air, it soon deliquesces from absorption of atmospheric moisture. It is very soluble in Alcohol with evolution of heat, and when the liquid is subjected to distillation, a highly concentrated spirit passes over, leaving a viscid mass which crystallizes on cooling, and contains nearly sixty per cent. of Alcohol in a state of loose chemical combination with the Chloride.

Pure dry Chloride of Calcium is an expensive salt, but a common quality, sufficiently good for the use above described, may be obtained at a lower price.

CALCIUM, IODIDE OF.

Formula, $CaI_2 = 294$.

This salt, useful for the preparation of some other Iodides, may be obtained either by saturating Hydriodic Acid with Carbonate of Lime, or by digesting Iodine with metallic Iron and Water until the liquid is purely green, then adding excess of Lime and filtering off the solution from the precipitate and evaporating.

CAMPHOR.

Formula, $C_{20}H_{16}O_2 = 152$.

This substance is obtained by distillation from the *camphor laurel* of China and Japan. When a small

piece is added to solutions of Gelatine, Albumen, Tannin, &c., it tends to prevent them from decomposition and mould.

CANADA BALSAM

Is a kind of inspissated turpentine obtained from a species of fir tree. In Photography it is used for cementing the components of Achromatic lenses, and when dissolved in Benzole for rendering paper highly translucent.

CAOUTCHOUC.

This substance, known also as India-rubber, is the inspissated milky juice of trees growing in South America and the East Indies. It is insoluble in water and in Alcohol.

Chloroform is the most perfect solvent for Caoutchouc, and leaves it unchanged on evaporation. Benzole also acts upon it. Mineral Naphtha takes it up on applying heat, but the residue after evaporation is sticky.

By combination with Sulphur, Caoutchouc undergoes a change of properties, familiar to us in the article sold as *vulcanized India-rubber*.

CARBOLIC ACID.

Formula, $C_6H_6O = 94$.

Like Creasote, this substance is derived from wood or coal tar. It is a powerful antiseptic—or preventive of putrefaction—more so than Creasote. For this purpose a very minute quantity added to Albumen, &c., will prevent decay or mould.

CASTOR OIL.

This oil is extracted from the seeds of *Ricinus communis*, or Palma Christi, both of which are cultivated in warm climates.

In Photography it is used in a small quantity to confer toughness on Collodion for transferring from the glass, and also to give the same property to Photographic varnishes.

CHARCOAL, ANIMAL.

Animal Charcoal is obtained by heating animal substances, such as bones, dried blood, horns, etc., to redness, in close vessels, until all volatile empyreumatic matters have been driven off, and a residue of Carbon remains. When prepared from bones, it contains a large quantity of inorganic matter in the shape of Carbonate and Phosphate of Lime. Animal charcoal is freed from these earthy salts by repeated digestion in Hydrochloric Acid; but unless very carefully washed it is apt to retain an acid reaction, and so to liberate free Nitric Acid when added to solution of Nitrate of Silver.

Properties.—Animal charcoal, when pure, consists solely of Carbon, and burns away in the air without leaving any residue: it is remarkable for its property of decolorizing solutions; the organic colouring substance being separated, but not actually *destroyed*, as it is by Chlorine employed as a bleaching agent. This power of absorbing colouring matter is not possessed in an equal degree by all varieties of Charcoal, but is in great measure peculiar to those derived from the animal kingdom.

CHLORINE.

Symbol, Cl = 35·5.

Chlorine is an element, found abundantly in Nature, combined with metallic Sodium in the form of Chloride of Sodium, or Sea-Salt.

Preparation.—By the action of Hydrochloric Acid on a natural product known as Binoxide of Manganese, MnO_2. The reaction may be thus represented :—

$$MnO_2 + 4HCl = MnCl_2 + H_2O + 2Cl.$$

Properties.—Chlorine is a greenish-yellow gas of a pungent and suffocating odour: soluble to a considerable

extent in water, the solution possessing the odour and colour of the gas. It is nearly $2\frac{1}{2}$ times as heavy as a corresponding bulk of atmospheric air.

Chemical properties.—Chlorine belongs to a small natural group of elements which contains also Bromine, Iodine, and Fluorine. They are characterized by having a strong affinity for Hydrogen, and also for the metals; but are comparatively indifferent to Oxygen. Many metallic substances actually undergo *combustion* when projected into an atmosphere of Chlorine, the union between the two taking place with extreme violence. The characteristic bleaching properties of Chlorine gas are explained in the same manner:—Hydrogen is removed from the organic substance, and in that way the structure is broken up and the colour destroyed.

Chlorine is more powerful in its affinities than either Bromine or Iodine. The salts formed by these three elements are closely analogous in composition, and often in properties. Those of the Alkalies, Alkaline Earths, and many of the Metals, are soluble in water; but the Silver salts are insoluble; the Lead salts sparingly so.

The combinations of Chlorine, Bromine, Iodine, and Fluorine, with Hydrogen, are acids, which by combination with bases form *haloid* salts and water.

The test by which the presence of Chlorine is detected, in its free state, or in its soluble metallic compounds, is *Nitrate of Silver*; it gives a white curdy precipitate of Chloride of Silver, insoluble in Nitric Acid, but soluble in Ammonia. The solution of Nitrate of Silver employed as the test must not contain Iodide of Silver, since this compound is precipitated by dilution.

CHLOROFORM.

Formula, $C_2HCl_3 = 119{\cdot}5$.

This volatile liquid is obtained by the action of Chloride of Lime upon dilute Alcohol. It does not mix with water, but is very soluble in Spirit.

Chloroform is the best solvent known for Caoutchouc, and it also dissolves Gutta-percha readily. Amber and many other resins are more or less soluble in Chloroform; and this solvent is well suited for the preparation of Photographic Varnishes, from its volatility, and from its having no solvent power on any of the varieties of Collodion films, some of which would be dissolved by an Alcohol Varnish.

CHROMIUM.

Symbol, Cr = 26·3.

Chromium is a metallic element found in the state of Oxide combined with Oxide of Iron in the mineral termed Chrome Ironstone. Its most important Oxides are the basic Oxide Cr_2O_3 and Chromic Acid, CrO_3.

Chromate of Potash, the source of all the preparations of Chromium, is obtained from the ore by fusing it for a long time with Nitrate of Potash; the latter imparts Oxygen, which changes Cr_2O_3 into two atoms of CrO_3, which with the Potash forms Chromate: this is afterwards dissolved out and crystallized.

The Chromate acidified with Nitric Acid yields the Bichromate of Potash, which is purified by crystallization.

CITRIC ACID.

$$H_3,C_6H_5O_7 + H_2O = 210.$$

This acid is derived from the juice of lemons and other fruits. It is made to undergo a short fermentation in order that impurities may subside. It is then neutralized with chalk, by which Citrate of Calcium, an insoluble compound, is formed. After washing, this Citrate is decomposed with dilute Sulphuric Acid; the solution is evaporated and left to crystallize. The pro-

duct may be purified by another process; but for Photographic work this is not necessary.

Citric Acid is a powerful retardent to the action of the developer, much more so than Acetic Acid. Hence, in hot weather it is much used; and, for the same reason, it is also very useful when intensifying a Negative, as it tends to keep the shadows clear.

A small proportion of Citric Acid may be added with great advantage to the Nitrate solution for sensitizing Positive paper, when there is too much tendency exhibited by the paper to print of a pale slaty tone.

CYANOGEN.

Formula, CN = 26. Symbol, Cy.

Cyanogen is a very remarkable *compound*, which behaves in many respects like the *elements*, Chlorine, Bromine, and Iodine. Like them it unites with Hydrogen to form an Acid, Hydrocyanic or Prussic Acid; and like them it combines with metals to form *Haloid* Salts. Cyanide of Silver, AgCN or AgCy, much resembles Chloride of Silver in properties.

Cyanogen has a capacity for forming complex compounds with certain metals, in which the metals can no longer be discovered by the usual tests; thus Iron for example enters into the composition of the Ferrocyanides, but no ordinary test would discover it.

Cyanogen in the uncombined state is a gas; it cannot be formed directly from its elements, Carbon and Nitrogen, but may easily be procured by heating one of its compounds, Cyanide of Mercury, $HgCy_2$ = Hg + 2Cy.

ETHER, SULPHURIC.

Formula, $C_4H_{10}O = 74$.

It will be altogether unnecessary to describe the manufacture of this compound, because it can only be

prepared properly by those thoroughly conversant with the process on a large scale. Sufficient be it to point out the means of ascertaining when one has got this most important Photographic material in a state fit for his purpose.

The first test is that of smell. If the Ether smells of Methyl or Wood Spirit, reject it without going farther; but if it does not, proceed to test it farther with Tincture of Iodine. Put one drop of the latter into, say, an ounce of the Ether. If the resulting colour is discharged after a few hours, that Ether is not to be trusted to, as it certainly contains too much Methyl. The other test is for Specific Gravity, which should range from 720 to not more than 730.

When pure Ether is exposed to light it *ozonizes* or becomes acid, and is liable to decompose the Iodides &c. with which it has afterwards to come in contact. Hence it should always be kept in a dark and, for another reason, in a cool place.

Water is detected in Ether by the turbidity which it causes when the latter is dropped into Spirits of Turpentine; if no water is present, the two mix perfectly.

An *ozonized* condition of Ether is at once detected, on agitating it with a little of a solution of Iodide of Potassium in Water or Alcohol, by its colouring the latter more or less yellow from the liberation of Iodine. The difference between bad and good Ether is seen most evidently after long keeping. Supposing white light to be excluded, a pure sample of Ether may be placed in a bottle, only half full, and at the expiration of two or three months it will scarcely become coloured on the first addition of Iodide of Potassium. Ether only partially purified will often stand the test of Iodide of Potassium when freshly distilled, but it will soon acquire the property of liberating Iodine when it is stowed away for keeping.

ETHER, METHYLATED.

This preparation is largely, indeed almost universally, used in the manufacture of the Collodions of the present day. When properly rectified and purified it answers very well, and, being so much cheaper than the Ethylic Ether, has almost superseded that produced from pure Alcohol. Its only bad tendencies are to disarrange the Nitrate Bath, and by its acrid fumes to affect the eyes of the operator when coating his glasses with Collodion.

ETHER, METHYLIC.

Formula, $C_2H_6O = 46$.

This Ether bears the same relation to Pyroxylic Alcohol or Wood Spirit, that ordinary Ether bears to Alcohol from Wine. It is a gaseous substance, which dissolves to a certain extent in water, but more abundantly so in Alcohol or Ether.

GALLIC ACID.

Formula, $H,C_7H_5O_5 = 170$.

Gallic Acid is obtained from the Tannic Acid by a species of fermentation. The powdered galls mixed with water, or their infusion, is left for some weeks, during which it becomes mouldy. Oxygen is absorbed and Carbonic Acid is given off, and Gallic Acid is deposited in abundance. The mouldy paste is squeezed, to get rid of foreign matters, and then boiled in water, which on cooling deposits the Gallic Acid. By digestion with Animal Charcoal, and recrystallization, it is obtained pure.

Gallic Acid, like Tannic Acid, gives an intensely blue black colour with salts of Peroxide of Iron, but it differs from the latter in giving no precipitate with Gelatine.

GELATINE.

This is a nitrogenized organic substance somewhat analogous to Albumen, but differing from it in properties. It is obtained by subjecting bones, hoofs, horns, calves' feet, &c., to the action of boiling water. The jelly formed on cooling is termed *size*, or, when dried and cut into slices *glue*. Gelatine, as it is sold in the shops, is a pure form of Glue. *Isinglass* is gelatine prepared, chiefly in Russia, from the air bladders of certain species of sturgeon.

Properties of Gelatine.—Gelatine softens and swells up in cold water, but does not *dissolve* until heated; the hot solution, on cooling, forms a tremulous jelly. One ounce of cold water will retain about three grains of Isinglass without gelatinizing; but much depends upon the temperature, a few degrees greatly affecting the result. The solution forms an insoluble precipitate with Tannic Acid, which has the composition of Leather.

When long boiled in water, and especially in presence of an acid, such as the Sulphuric, Gelatine undergoes a peculiar modification, and the solution loses either partially or entirely its property of solidifying to a jelly.

GLYCERINE.

Formula, $C_3H_8O_3 = 92$.

Fatty bodies are resolved by treatment with an alkali into an acid, which combines with the alkali, forming a *soap*, and Glycerine, which remains in solution.

Pure Glycerine, as obtained by Price's patent process of distillation, is a sweet viscid liquid of sp. gr. about 1·23; miscible in all proportions with water and Alcohol. It is neutral to test-paper. It has little or no action upon Nitrate of Silver in the dark, and reduces it very slowly even when exposed to light. Glycerine has been used as a preservative for keeping wet Collodion films from drying during long exposures.

GOLD, CHLORIDE OF.

Formula, $AuCl_3 = 303{\cdot}5$.

There are two Chlorides of Gold—viz., the Protochloride and the Terchloride. The latter is the one used in Photography. It is prepared by dissolving gold in *aqua regia* or Nitro-Hydrochloric Acid.

Absolutely pure Chloride of Gold can only be made from the pure metal, but as purity is not an essential for Photographic purposes, the following method of making it from standard gold coin, which also applies to the pure metal, will be found convenient. The Australian gold coins, in which the alloy is silver, are preferable to those of the English mint, inasmuch as the silver is left in the shape of undissolved chloride, which can be afterwards filtered out, whereas copper is much more difficult to get rid of. The mode of procedure is as follows :—

Mix in a rather tall and thin German beaker two fluid drams of Nitric with one ounce of Hydrochloric Acid. Unless the acids are very strong the addition of water will be unnecessary. Place in the mixture, say an Australian soverign, and apply a gentle heat, which should be continued until solution is complete. A water bath or a warm hob will give sufficient heat to commence and continue the action. In most cases the above proportion of acids will be sufficient to dissolve the sovereign if the gentle heat is continued; but if not add a little more mixed acid. A great excess of acid should be avoided, because it renders their neutralization or their subsequent elimination more difficult.

When solution of the gold is complete there will remain a precipitate of Chloride of Silver arising from the alloy. Dilute down, say with six ounces of distilled water, neutralize the excess of acids with powdered chalk, and filter into a stock bottle. But in order to avoid the least trace of waste rinse out the beaker with two ounces more of distilled water, which pass through

the filter into the stock bottle. Repeat the rinsing, &c. Thus we have the whole or nearly the whole of the gold in a sovereign converted into Chloride of Gold fit for Photographic purposes. It is advisable to keep this neutral solution of Chloride in the dark, because light has the effect of causing a partial reduction of the metallic element.

As a sovereign contains 113 grains of pure gold it is easy to calculate that, if waste is avoided, it will yield 174 grains of Chloride.

Supposing then the Chloride of Gold thus made from a sovereign is diluted, say with ten ounces of distilled water, each fluid ounce will contain seventeen grains of the Chloride, leaving four grains to be laid to the account of waste, or a light sovereign.

GOLD, HYPOSULPHITE OF.

Formula, $Au_2S_2O_3 = 506$.

This salt, which is produced by the reaction of Chloride of Gold on Hyposulphite of Soda, is now rarely employed in Photography. In former times it was much used for toning Daguerreotype images, and went under the name of "Sel d'Or."

Being a very unstable substance it is totally unfitted for toning Photographic paper prints, for which purpose it has been sometimes recommended.

GUMS.

These may be shortly described as exudations from various kinds of trees. They are all more or less soluble in water, and this distinguishes them from "resins," which are insoluble in that menstruum.

In Photography some of them are used as pastes for mounting Photographs, and dilute in solution as preservatives or organifiers in the dry Collodion processes. The only drawback to their employment for the latter

purpose is their tendency, when conjoined with Collodion, to cause blistering of the film during or after development.

Gum Arabic may be considered the best type of that class of substances called "*gums*."

HYDROBROMIC ACID.

Formula, HBr = 81.

This is prepared by decomposing Bromide of Potassium with a concentrated solution of Phosphoric Acid, or by decomposing Bromide of Phosphorus by means of a small quantity of water.

HYDRIODIC ACID.

Formula, HI = 128.

This is a gaseous compound of Hydrogen and Iodine, corresponding in composition to the Hydrochloric Acid. It cannot, however, from its instability, be obtained in the same manner, since, on distilling an Iodide with Sulphuric Acid, the Hydriodic Acid first formed is subsequently decomposed by the Sulphuric Acid. An aqueous solution of Hydriodic Acid is easily prepared by passing Sulphuretted Hydrogen gas through water standing over powdered Iodine, until the liquid, which about the middle of the operation becomes very brown on shaking, from solution of excess of Iodine, is *just* decolorized again. Sulphur separates out abundantly, and can be removed either by filtering or decantation. The solution ought not to smell of Sulphuretted Hydrogen, or blacken paper dipped in Acetate of Lead or Nitrate of Silver, held over it.

Hydriodic Acid gas is very soluble in water, yielding a strongly acid liquid. The solution, colourless at first, soon becomes brown from liberation of free Iodine. It may be restored to its original condition by adding solution of Sulphuretted Hydrogen, and allowing Sulphur to subside.

HYDROCHLORIC ACID.

Formula, HCl = 36·5.

Hydrochloric Acid is a volatile gas, which may be liberated from most of the salts termed Chlorides by the action of Sulphuric Acid.

It is abundantly soluble in water, forming the liquid Hydrochloric or Muriatic Acid of Commerce. The most concentrated solution of Hydrochloric Acid has a sp. gr. 1·2, and contains about 40 per cent. of gas; that commonly sold is somewhat weaker, sp. gr. 1·14 to 1·16, containing about 28 per cent. real acid.

Pure Hydrochloric Acid is colourless, and fumes in the air. The yellow colour of the commercial acid depends upon the presence of traces of Perchloride of Iron, or of organic matter; commercial Muriatic Acid also often contains free Chlorine and Sulphuric Acid.

HYDROGEN, PEROXIDE OF.

Formula, HO = 17.

This curious compound, now more usually known under the name of Hydroxyl, was discovered by Thénard in the year 1818. It is a powerful oxidizing agent, and is also a reducing agent. In virtue of its former property, it has been recommended as a very convenient solution for converting the last traces of injurious Hyposulphites in Photographic prints into innocuous Sulphates. This it does by oxidizing the Hyposulphites. But, unfortunately, it acts in two ways; first it oxidizes, and then reduces them.

HYDROSULPHURIC ACID.

$H_2S = 34$.

This gas, also known under the name of Sulphuretted Hydrogen, is usually prepared by the action of dilute

Sulphuric Acid on Sulphide of Iron. Cold water takes up about three times its volume of this gas, and the solution is slightly acid to litmus paper. In Photography it is chiefly used for reducing Silver from solutions of the salts of that metal. This it effects by throwing down Sulphide of Silver, which is again converted into the metal by fusion.

It is most important that this substance should not be used in the dark room, as the fumes arising from it would destroy all chance of good Photographic work with the salts of Silver.

IODINE.

Symbol, I = 127.

Iodine is chiefly prepared at Glasgow, from *kelp*, which is the fused ash obtained on burning seaweeds. The waters of the ocean contain minute quantities of the Iodides of Sodium and Magnesium, which are separated and stored up by the growing tissues of the marine plant.

In the preparation, the mother-liquid of kelp (which is the liquid that remains after most of the salts, which contain no Iodine, have been separated by crystallization) is distilled at a gentle heat with a certain proportion of Sulphuric Acid and Binoxide of Manganese.

The Iodine sublimes in purple vapours, which condense to black crystals.

Iodine has a bluish-black colour and metallic lustre: it stains the skin yellow, and has a pungent smell, like diluted Chlorine. It is extremely volatile when moist, boils at 347°, and produces dense violet coloured fumes, which condense in brilliant plates. Specific gravity, 4·946. Iodine is very sparingly soluble in water, 1 part requiring 7000 parts for perfect solution; even this minute quantity, however, tinges the liquid of a brown colour. Alcohol and Ether dissolve it more

abundantly, forming dark-brown solutions. Iodine also dissolves freely in solutions of the alkaline Iodides, such as the Iodide of Potassium, of Sodium, and of Ammonium.

Iodine possesses the property of forming a compound of a deep blue colour with starch. In using this as a test, it is necessary first to liberate the Iodine (if in combination) by means of Chlorine, avoiding an excess, or by means of Nitric Acid saturated with Peroxide of Nitrogen. The presence of Alcohol or Ether interferes to a certain extent with the result.

IRON, ACETATE OF.

Formula, $FeC_2H_3O_2 = 115$.

There are two Acetates of Iron, a Protacetate, which is nearly colourless, and a Peracetate, which is red; the former only is used in Photography.

A solution of the Protacetate containing a slight excess of the Sulphate, but sufficiently pure for Photographic purposes, may be made by dissolving 12 grains of Protosulphate of Iron and 12 grains of crystallized Acetate of Lead, each in half an ounce of water, mixing, and filtering from the white deposit, which is Sulphate of Lead. The solution is very unstable, and soon deposits a reddish Subsalt, or if free Acetic Acid be present, it assumes a red colour.

A mixture of Acetate of Soda with Protosulphate of Iron, six grains of the former and twelve grains of the latter to an ounce of water, acts in Photography very much in the same manner as the pure solution of the Acetate.

IRON, AMMONIO-CITRATE OF.

This beautiful pharmaceutical preparation is a basic salt containing Citric Acid in union both with Ammonia and with Peroxide of Iron. It is met with in the form

of thin transparent-brown scales, produced by drying a syrupy solution on warm plates.

The reaction of certain tests upon the Ammonio-Citrate and also upon the Ammonio-Tartrate of Iron, is peculiar. Free Ammonia, which usually throws down a red Sesquioxide from the Persalts of Iron, produces no deposit with these compounds; and Ferrocyanide of Potassium, which usually precipitates Prussian blue, simply produces a purple colour; the blue precipitate is, however, obtained on *acidifying* the liquid. The presence of the vegetable acid and the basic character due to Ammonia are the causes of these anomalies.

IRON, AMMONIO-SULPHATE OF.

Formula, $Fe(NH_4)_2(SO_4)_2 + 6H_2O = 392$.

This is a double salt of iron prepared by mixing equivalent proportions of Protosulphate of Iron and Sulphate of Ammonia. Take 139 parts of Protosulphate of Iron and 75 of Sulphate of Ammonia, dissolve them in a minimum of water, and set aside in an evaporating dish till the double salt crystallizes. It has been recommended to use this salt as a developer instead of the plain Protosulphate, chiefly on account of its greater stability. It possesses no other advantages.

IRON, OXALATE OF (Ferrous Oxalate).

Formula, $FeC_2O_4 = 144$.

This salt may be prepared by dissolving 2 ounces of Ferrous Sulphate in 30 ounces of water, and 396 grains of Oxalic Acid in 15 ounces of water, and mixing the two solutions. The Ferrous Oxalate is slowly precipitated. After which the clear liquid is decanted and the precipitate washed and dried.

IRON, PROTOSULPHATE OF.

Formula, $FeSO_4 + 7H_2O = 278$.

This salt, sometimes called copperas or green vitriol, is obtained by acting on iron wire or filings with dilute Sulphuric Acid, evaporating and crystallizing. When pure, the crystals are of a fine bluish green colour, free from red stains, and in the form of oblique rhombic prisms. In dry air they effloresce, but in moist air they become partially oxidized into a per-salt and assume a red colour.

Protosulphate of Iron forms double salts with the Sulphates of Ammonia and Potash. Its aqueous solution absorbs Binoxide of Nitrogen from the air and becomes of a deep brown colour. As Binoxide of Nitrogen is itself a reducing agent, it has been erroneously supposed by some that this changed solution is a more energetic developer than the plain Photosulphate.

IRON, PERCHLORIDE OF.

Formula, $Fe_2Cl_6 = 325$.

There are two Chlorides of Iron, corresponding in composition to the Protoxide and the Sesquioxide respectively. The Protochloride is very soluble in water, forming a green solution, which preciptates a dirty white Protoxide on the addition of an alkali. The Perchloride, on the other hand, is dark-brown, and gives with alkalies a reddish-brown precipitate of Peroxide.

Perchloride of Iron may be obtained in a state of purity by heating Iron wire in excess of Chlorine; it condenses in the shape of brilliant and iridescent brown crystals, which are volatile, and dissolve in water, the solution being acid to test-paper; a more easy mode of preparing the solution, however, is by digesting Hydrochloric Acid with excess of Peroxide of Iron. It is soluble in Alcohol, forming the Tinctura

Ferri Sesquichloridi of the Pharmacopœia. Commercial Perchloride of Iron ordinarily contains an excess of Hydrochloric Acid.

IRON, IODIDE OF.

Formula, $FeI_2 = 310$.

Iodide of Iron is prepared by digesting an excess of Iron filings with pulverized Iodine and Water. It is very soluble in Water and in Alcohol, but the solution rapidly absorbs Oxygen, and deposits Peroxide of Iron; hence the importance of preserving it in contact with metallic Iron, with which the separated Iodine may recombine. By very careful evaporation, hydrated crystals of Protoiodide may be obtained, but the composition of the solid salt usually sold under that name cannot be depended on.

IRON, SESQUIOXALATE OF (Ferric Oxalate).

Formula, $Fe_2(C_2O_4)_3 = 376$.

This salt is prepared by dissolving the Hydrated Peroxide in a solution of Oxalic Acid. It is very soluble in water, and has several applications in Photography, based upon its sensitiveness to light, by which it is reduced to the Ferrous Oxalate. Its chief use is in the Platinotype Printing Process, in which paper, prepared with a mixture of Ferric, Oxalic and Potassic Chloroplatinite, is exposed to light under a negative, when an image is formed in Ferrous Oxalate. The picture is floated on a hot solution, consisting chiefly of neutral Potassic Oxalate, by which the Ferrous Oxalate is dissolved, and acting instantly upon the Platinic Salt with which it is in contact, the latter is reduced, and an image formed in Metallic Platinum.

KAOLIN, OR CHINA CLAY.

This is employed by Photographers to decolorize solutions of Nitrate of Silver which have become brown from the action of Albumen or other organic matters.

LEAD, ACETATE OF.

$$Pb(C_2H_3O_2)_2 + H_2O = 343.$$

The neutral Acetate of Lead is a very abundant substance in commerce, and is known as *Sugar of Lead.* It is prepared by digesting Oxide of Lead in Pyroligneous or Acetic Acid, and crystallizes in acicular masses.

Acetate of Lead is easily soluble in cold water, but the solution is usually milky, either from the presence of a little Carbonate mixed with the Acetate, or from Carbonic Acid or Carbonate of Lime in the water used.

When a little of this salt is added to the Gallic Acid *developer* for paper Negatives or Positives, it exercises a marked effect in forwarding the development. The rationale is not known, but the fact remains.

LIME, CHLORIDE OF.

The exact chemical composition of this substance is a subject of dispute among chemists. It emits the peculiar odour of Hypochlorous Acid when exposed to the air, and at the same time absorbs Carbonic Acid.

In Photography it is sometimes used in the Gold toning bath to neutralize the acidity of the solution; but it must be so used with great discretion, otherwise the Chlorine which escapes attacks the silver image and greatly weakens it.

On account of its powerful oxidizing properties, a solution of this salt has been recommended for eliminating the last traces of soluble Hyposulphite from washed Photographic prints. This it effects in the same way as Peroxide of Hydrogen, by oxidizing the Hyposulphite into an innocuous Sulphate. It is doubtful, however, whether the advantage gained will counterbalance the disadvantage of an enfeebled print.

The so-called Chloride of Lime is an excellent substance for removing silver stains from the hands, linen, &c. Make up a little dry Chloride into a paste, with water

acidulated with any acid, and apply to the stains by hard rubbing. They will quickly disappear. Afterwards wash with Hyposulphite of Soda solution, which absorbs the disagreeable Chlorine fumes.

LITHIUM, IODIDE OF.

Formula, $Li + 6Aq = 242$.

Lithium is one of the rarer elements, found in the mineral kingdon, and the basic reactions of its Oxide are so strong that it takes its place with the alkalies Potash and Soda. Metallic Lithium, though a metal, is the lightest solid body known, its density being little more than one-half of that of water.

Iodide of Lithium has been proposed for Photographic use, being more easily soluble in Alcohol than Iodide of Potassium. Its deliquescent nature, however, is an objection, as also is the difficulty and expense of obtaining it commercially in a pure state. A solution of the Iodide may be prepared by mixing equivalent proportions of crystallized Sulphate of Lithia and Iodide of Calcium in concentrated aqueous solution, evaporating to dryness over Sulphuric Acid *in vacuo*, and exhausting the dry residue with Alcohol of ·805. Iodide of Calcium is preferable to Iodide of Barium, in consequence of the latter being more frequently contaminated with an excess of base.

LITMUS.

Litmus is a vegetable substance prepared from various *lichens*, which are principally collected on rocks adjoining the sea. The blue colouring-matter is extracted by a peculiar process, and is afterwards made up into a paste with chalk, plaster of Paris, etc.

Litmus occurs in commerce in the form of small cubes of a fine violet colour. In using it for the preparation of test-papers, it is digested in hot water, the solution concentrated at a gentle heat, and sheets of porous paper

soaked in the blue liquid so formed. The red papers are prepared at first in the same manner, but are afterwards placed in water which has been rendered faintly acid with Sulphuric or Hydrochloric Acid. Papers are prepared also of a *purplish* tint, which becomes full blue with alkalies, and bright red with acids.

MAGNESIUM.

Symbol, Mg = 24.

This is a silver-white metal of crystalline structure, and somewhat brittle. It is obtained from the Chloride by several methods which need not be described here.

If kept in dry air this metal is not altered, but, in damp air, it soon becomes covered with a film of Hydrate of Magnesium.

Its only use in Photography is for the purpose of illumination, as it emits a most dazzling light when burnt in air or Oxygen. For this purpose it is sold in the form of wire or ribbon. The light emitted is supposed to be more *actinic* than any other form of artificial illumination.

An ingenious lamp with a reflector has been devised, which facilitates the production of a regular and constant flame from the burning metal. The product of the combustion is Magnesia.

The Bromide and Iodide of Magnesium are objectionable in Photography by reason of their great affinity for water, and their liability to decomposition.

MERCURY, CHLORIDE OF
(Formerly Bichloride).

Formula, $HgCl_2 = 271$.

This salt, also called Corrosive Sublimate, and often *Bichloride of Mercury* (the atomic weight of Mercury being doubled), may be formed by heating Mercury in excess of Chlorine, or, more economically, by subliming

a mixture of Sulphate of Mercury and Chloride of Sodium.

Properties.—A very corrosive and poisonous salt, usually sold in semi-transparent, crystalline masses, or in the state of powder. Soluble in 16 parts of cold, and in 3 of hot water; more abundantly so in Alcohol, and also in Ether. The solubility in water may be increased by the addition of free Hydrochloric Acid, or of Chloride of Ammonium.

This salt is sometimes used as an intensifier for Negatives. A saturated aqueous solution is poured over the image until the latter becomes of a whitish grey colour. The film is then washed, and treated with a one-grain solution of Iodide of Potassium until the image assumes a green tone, which is very non-actinic. Negatives so treated, after repeated exposures to light, become too dense.

NAPHTHA.

This name is applied to several liquids sold in commerce. First, *Wood Naphtha*, often used for burning in lamps, which is the same as Pyroxylic Spirit or Methylic Alcohol, *q. v.*; second, *Coal Naphtha*, a volatile liquid which distils over in the process of manufacturing gas; and, thirdly, *Mineral Naphtha*, found in the soil of certain places in Europe and Asia, and recently very abundantly in Canada and Pennsylvania, in America.

The two latter substances, to which the name of Naphtha ought to be restricted, possess the same leading characteristic, in that they are Hydrocarbons, burning with a bright, smoky flame; they do not mix with water, and they dissolve Caoutchouc, in all which respects they differ from "Wood Naphtha."

NITRIC ACID.

Formula, $HNO_3 = 63$.

Nitric Acid, or *Aqua-fortis*, is prepared by adding Sulphuric Acid to Nitrate of Potash, and distilling the

mixture in a retort. Sulphate of Potash and free Nitric Acid are formed, the latter of which, being volatile, distils over in combination with one atom of water previously united with the Sulphuric Acid.

Anhydrous Nitric Acid is a solid substance, white and crystalline, but it cannot be prepared except by an expensive and complicated process.

The strongest *liquid* Nitric Acid contains 1 atom of water, and has a sp. gr. of about 1·5; if perfectly pure, it is colourless, but usually it has a slight yellow tint, from partial decomposition into Peroxide of Nitrogen: it fumes strongly in the air.

The strength of commercial Nitric Acid is subject to much variation. An acid of sp. gr. 1·42, containing about 4 atoms of water, is often met with. If the specific gravity is much lower than this (less than 1·36), it will scarcely be adapted for the preparation of Pyroxyline. The yellow *Nitrous Acid*, so called, is a strong Nitric Acid, partially saturated with the brown vapours of Peroxide of Nitrogen: it has a high specific gravity, usually about 1·45, but this is deceptive, being caused in part by the presence of the Peroxide. On mixing with Sulphuric Acid, the colour disappears, a compound being formed which has been termed a *Sulphate of Nitrous Acid.*

Nitric Acid is a powerful oxidizing agent; it attacks all the common metals, with the exception of Gold and Platinum. Metals dissolving in acids usually derive the necessary amount of Oxygen from the water, Hydrogen being given off; but when Nitric Acid is the solvent, Oxygen is derived *from it*, and N_2O_2 or N_2O_3 or N_2O_4 escapes. Animal substances, such as the cuticle, nails, etc., are tinged of a permanent yellow colour, and are deeply corroded by a prolonged application. Nitric Acid forms a numerous class of salts, *all of which are soluble in water;* hence its presence cannot be determined by any precipitating reagent, in the same manner as that of Hydrochloric and Sulphuric Acid.

The principal impurities in commercial Nitric Acid

are *Chlorine* and *Sulphuric Acid;* also Peroxide of Nitrogen, which tinges the acid yellow, as already described. Chlorine is detected by diluting the acid with an equal bulk of distilled water, and adding a few drops of Nitrate of Silver—*a milkiness*, which is Chloride of Silver in suspension, indicates the presence of Chlorine. In testing for Sulphuric Acid, dilute the Nitric Acid as before, and drop in *a single drop* of solution of Chloride of Barium; if Sulphuric Acid be present, an insoluble precipitate of Sulphate of Baryta will be formed.

A convenient form of acid for preparing Pyroxyline is the Nitric Acid of 1·45. The question has been asked, why so concentrated an acid is recommended, seeing that it is afterwards to be diluted with water? There are two reasons; first, because this acid is cheaper in the end, and perhaps more uniform than a weaker acid; and secondly, it is important that both the Sulphuric and Nitric Acid should be as strong as possible, in order to allow of the use of sufficient water to raise the temperature of the resulting Nitro-Sulphuric Acid at once to the proper point, and so to obviate the necessity of employing artificial heat.

NITROGEN.

Symbol, N = 14.

Nitrogen is an element, existing as a gas, in the free state. Our atmosphere consists of a *mixture* of the two elements Nitrogen and Oxygen, in the proportion of 4 volumes of the first with 1 volume of the second.

Nitrogen, when free, is remarkably devoid of sensible properties, and can scarcely be made *directly* to unite with any element. Its compounds are, however, numerous and important, Nitric Acid, HNO_3, being one of its oxides; Ammonia, NH_3, is its compound with Hydrogen, and Cyanogen, CN, its compound with Carbon.

NITRO-GLUCOSE.

When 3 fluid ounces of cold Nitro-Sulphuric Acid, consisting of 2 ounces of Oil of Vitrol and 1 ounce of highly concentrated Nitric Acid, are mixed with 1 ounce of finely powdered Cane sugar, there is formed at first a thin, transparent, pasty mass. If it is stirred with a glass rod for a few minutes without interruption, the paste coagulates as it were, and separates from the liquid as a thick tenacious mass, aggregating into lumps, which can easily be removed from the acid mixture.

This substance is a *substitution* compound, and is derived from Sugar as Gun-cotton is from Cotton, by the displacement of a part of the H in Sugar by NO_2. It has a very acid and intensely bitter taste. Kneaded in warm water until the latter no longer reddens litmus-paper, it acquires a silvery colour and a beautiful silky lustre. When dissolved in Collodion, it *ozonizes* the Ether on keeping for some months, and hence there is a rapid liberation of Iodine when the iodizer is added. Alkalies decompose Nitro-Glucose, evolving a smell of burnt sugar. The product lessens the sensitiveness of Collodion, but increases the intensity of the image.

NITRO-HYDROCHLORIC ACID.

This liquid is the Aqua Regia of the old alchemists. It is produced by mixing Nitric and Hydrochloric Acids; the Oxygen of the former combines with the Hydrogen of the latter, forming water and liberating Chlorine.

The presence of free Chlorine confers on the mixture the power of dissolving Gold and Platinum, which neither of the two acids possesses separately. In preparing Aqua Regia it is usual to mix one part, by measure, of Nitric Acid with four of Hydrochloric Acid, and to dilute with an equal bulk of water. The Application of a gentle heat assists the solution of the metal; but if the temperature rises to the boiling point, effervescence and loss of Chlorine takes place.

ORGANIC MATTER.

This term is often employed to designate varieties of non-volatile vegetable and animal substances of unknown composition, which are prone to change by absorption of Oxygen. Bodies which have a definite formula, however, are often included in the class of "Organic matters" if they easily pass by oxidation into ill-defined products. Thus the Sugar of Liquorice, which soon decomposes and becomes brown, may be referred to under that head; but a stable vegetable acid like Acetic Acid, or a neutral substance not readily oxidizable, such as Glycerine, although really organic in composition, would not usually be referred to by this term.

Organic matter of the kind above alluded to reacts upon Nitrate of Silver in presence of light, reducing it more or less perfectly to the metallic state, and becoming itself oxidized.

Carbon is essentially the organic element, as every organic body is a compound of Carbon.

OXYGEN.

Symbol, O = 16.

Oxygen gas is one of the elements; it is very abundantly distributed, both in the free state and in combination. In the former state it exists in our atmosphere, but *mixed* with four times its bulk of the elementary gas Nitrogen. Its compounds, as stated in Chapter I., are either acids, bases, or neutral bodies. It can be obtained in a state of almost perfect purity and in great abundance by heating the salt Chlorate of Potash to gentle redness in a flask or retort; Chloride of Potassium remains. This decomposition is rendered more easy by first mixing the powdered Chlorate with one-fourth of *well-dried*, and powdered, Black Oxide of Manganese.

OZONE.

Oxygen, in the state in which it usually exists in the atmosphere, exhibits no very powerful chemical properties at ordinary temperatures; thus, it has no action on Iodide of Potassium—it cannot displace the Iodine to combine with the Potassium. It appears, however, that Oxygen, though an element, is capable of taking on a more active form, in which condition it almost resembles Chlorine in its tendency to combine with bodies. In this state it instantly attacks Iodides of Potassium, Sodium, etc., forming Potash, Soda, etc., and setting Iodine free. To this modification of Oxygen the term Ozone has been applied, a name derived from ὄζω (*ozo*, I smell), on account of its having a remarkable odour.

Some organic bodies, as Ether and Spirits of Turpentine, have the power of converting a portion of the Oxygen of the air into Ozone, which they loosely retain. This condition of Ether can easily be produced by thrusting a red-hot wire* into the vapour in a bottle containing a little Ether. On shaking the bottle afterwards, and testing with a solution of Iodide of Potassium, Ozone will be indicated by the liberation of Iodine. This condition of Ether occurs spontaneously after a time; it may be got rid of by distillation from solid Potash.

PHOSPHORIC ACID.

Formula, $HPO_3 = 80$.

This acid in a diluted form is used in Willis's Aniline process. It may be prepared by pouring four fluid ounces of Nitric Acid and eight ounces of distilled water on six drachms of Phosphorus in a retort, and applying the heat of a sandbath. The distillation should proceed till the residue in the retort is of a syrupy

* No *flame* should ever be brought near an Ether bottle, for fear of an explosion.

consistence. The syrup is then poured into a platinum vessel, and heated to a dull red. On cooling, it concretes into a transparent mass, often assuming the crystalline form. This constitutes what is called Glacial Phosphoric Acid, which may be diluted to any extent.

POTASH.

Formula, $KHO = 56{\cdot}1$.

Potash, the Oxide of Potassium, is obtained from Carbonate of Potash by separating the Carbonic Acid by means of Caustic Lime. Lime is a more feeble base than Potash, but the Carbonate of Lime, being *insoluble* in water, is at once formed on adding Milk of Lime to a solution of Carbonate of Potash in not less than twelve parts of water.

Properties.—Usually met with in the form of solid lumps, or in cylindrical sticks, which are formed by melting the Potash and running it into a mould. It always contains one atom of water, which cannot be driven off by the application of heat.

Potash is soluble almost to any extent in water, much heat being evolved. The solution is powerfully alkaline, and acts rapidly upon the skin; it dissolves fatty and resinous bodies, converting them into soaps. Solution of Potash absorbs Carbonic Acid quickly from the air, and should therefore be preserved in stoppered bottles; the glass stoppers must be wiped occasionally, in order to prevent them from becoming immovably fixed by the solvent action of the Potash upon the Silica of the glass.

The Liquor Potassæ of the London Pharmacopœia has a sp. gr. of 1·063, and contains about 5 per cent. of real Potash. It is usually contaminated with *Carbonate* of Potash, which causes it to effervesce on the addition of acids; also, to a less extent, with Sulphate of Potash, Chloride of Potassium, Silica, etc.

POTASH, BICHROMATE OF.

Formula, $K_2Cr_2O_7 = 294{\cdot}6$.

This salt is largely manufactured for the use of calico printers, from a native compound of the oxides of Chromium and Iron. It occurs in fine orange-coloured crystals, which are soluble in about ten parts of water at 60° Fahrenheit.

There are two Chromates of Potash—a neutral Chromate, which is yellow and contains an atom of each constituent; and a Bichromate, orange-red, as before mentioned, and having two atoms of acid to one of base. The Chromic acid of Bichromate of Potash, in contact with organic bodies such as Gelatine, is decomposed by light, yielding up half its Oxygen to the organic body, and being itself reduced to a lower Oxide of Chromium.

The organic body thus oxidized, if previously soluble in water, is often, as in the case of Gelatine, rendered insoluble in water, and upon this fact are founded numerous Photographic processes.

POTASH, CARBONATE OF.

Formula, $K_2,CO_3 = 138{\cdot}2$.

The impure Carbonate of Potash, termed *pearlash*, is obtained from the ashes of wood and vegetable matter, in the same manner as Carbonate of Soda used to be prepared from the ashes of seaweeds. Salts of Potash and of Soda appear essential to vegetation—the former to land and the latter to sea plants—and are absorbed and appropriated by the living tissues of the plants. They exist in the vegetable structure combined with organic acids in the form of salts, Oxalate, Tartrate, etc., which, when burned, are converted into Carbonate.

Properties.—The Pearlash of commerce contains large and variable quantities of Chloride of Potassium,

Sulphate of Potash, etc. A purer Carbonate is sold, which is free from Sulphates, and with only a trace of Chlorides. Carbonate of Potash is a strongly alkaline salt, deliquescent, and soluble in twice its weight of cold water; insoluble in Alcohol, and employed to deprive it of water.

POTASH, NITRATE OF.

Formula, $KNO_3 = 101{\cdot}1$.

This salt, also termed *Nitre*, or *Saltpetre*, is an abundant natural product, found efflorescent upon the soil in certain parts of the East Indies. It is also produced artificially in what are called Nitre-beds.

There are different qualities of Nitre sold in commerce, some of which contain much Chloride of Potassium, detected on dissolving the Nitre in distilled water, and adding a drop or two of solution of Nitrate of Silver. This impurity is injurious when the Nitre is employed for Photographic use: in the manufacture of Pyroxyline it decomposes the Nitric Acid; and in the case of positive developing solutions, the presence of Chloride in the Nitre seems to produce a white cloudiness on the film.

A quality of Nitre which answers very well for making Pyroxyline can be obtained at the operative chemists' at one shilling per pound; it is often sold as pure Nitre, but usually contains sufficient Chloride to produce an opalescence with Nitrate of Silver; if the impurity is in larger quantity, and produces a decided precipitate with Nitrate of Silver, the sample must be rejected.

POTASSIUM, BROMIDE OF.

Formula, $KBr = 119{\cdot}1$.

Bromide of Potassium is prepared by adding Bromine to Caustic Potash, and heating the product, which is a

mixture of Bromide of Potassium and Bromate of Potash, to redness, in order to drive off the Oxygen from the latter salt. It crystallizes in anhydrous cubes, the Chloride and Iodide of Potassium; it is easy soluble in water, but very sparingly so in Alcohol; it yields red fumes of Bromine when acted upon by hot and strong Sulphuric Acid.

This salt is useful in Photographic processes on paper, but in Collodion it is liable to cause turbidity and spots.

POTASSIUM, CYANIDE OF.

Formula, $KCN = 65{\cdot}1$.

Cyanide of Potassium may be regarded either as a compound of Cyanogen and Potassium (*see* CYANOGEN), or as a salt, derived from Hydrocyanic, or "Prussic" Acid.

It is obtained from Ferrocyanide of Potassium by mixing eight parts of this salt, thoroughly dried, with three of dried Carbonate of Potash, and fusing in a covered earthen crucible. When effervescence has ceased, and Iron, which separates, has settled down, the clear liquid is poured off, and on cooling solidifies into the white mass known as Cyanide of Potassium. Thus obtained it is not quite pure, and, as sold in commerce, it often only contains about half its weight of true Cyanide; but the impurities present, of which Carbonate of Potash is the principal, do not produce any injurious effect beyond lessening the strength of the salt. It is highly poisonous, and, if treated with an acid, it gives off the very volatile and poisonous Hydrocyanic Acid, the vapour of which, incautiously inhaled, might cause fainting, or even death.

POTASSIUM, FLUORIDE OF.

Formula, $KF = 58{\cdot}1$.

Preparation.—Fluoride of Potassium is formed by

saturating Hydrofluoric Acid with Potash, and evaporating to dryness in a platinum vessel. *Hydrofluoric Acid* contains the element Fluorine combined with Hydrogen; it is a powerfully acid and corrosive liquid, formed by decomposing Fluor Spar, which is a *Fluoride of Calcium*, with strong Sulphuric Acid; the action which takes place being precisely analogous to that involved in the preparation of Hydrochloric Acid.

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF.$$

Properties.—A deliquescent salt, occurring in small and imperfect crystals. Very soluble in water; the solution acting upon glass in the same manner as Hydrofluoric Acid.

POTASH, OXALATE OF.

Formula, $K_2C_2O_4$.

Potassium Oxalate, or the Neutral Oxalate of Potash, which is now much employed in Photography as a solvent of Ferrous Oxalate for use as a developer, is prepared by neutralizing a solution of Oxalic Acid with Potassium Carbonate, and then evaporating and crystallizing. It is soluble in three parts of water. Those Photographers who prepare it for their own use rarely trouble themselves with crystallizing it, but allow it to remain in the liquid form.

POTASH, PERMANGANATE OF,

Formula, $K_2Mn_2O_8 = 316{\cdot}2$,

is a salt which has been recommended for destroying organic matter in the Nitrate of Silver bath. It acts as an oxidizing agent.

POTASSIUM, IODIDE OF.

Formula, $KI = 166{\cdot}1$.

This salt may be prepared by dissolving Iodide in a

solution of Potash until it assumes a brown colour. Iodide of Potassium and Iodate of Potash are thus formed, but by evaporation and heating to redness, the latter salt parts with its Oxygen, and is converted into Iodide of Potassium. The salt is then redissolved, filtered, and allowed to crystallize.

Iodide of Potassium may contain several *incidental* impurities from carelessness in the manufacture. If Carbonate, Iodate, or Sulphate be present, solution of Chloride of Barium will detect them. In the two former instances the precipitate dissolves on the addition of a single drop of *pure* dilute Nitric Acid, but in the latter case it is insoluble.

A simple test for Carbonate of Potash, which is the most objectionable impurity, is to dissolve the Iodide in about three times its weight of Lime water; a turbidity will indicate the presence of Carbonate.

The mere fact of reddened litmus-paper becoming blue in solution of Iodide of Potassium is no proof of impurity, since the finest crystals which can be obtained have an alkaline reaction. But if an Alcoholic solution of the Iodide remains quite colourless when exposed for several days to a strong light, it is almost certain that an excess of alkali is present; the chemically pure Iodide of Potassium is generally decomposed by light, and assumes a faint straw-yellow tint, returning, however, to its colourless condition on putting the bottle again in a dark place.

Iodide of Potassium may, when required, be purified by recrystallizing it from Spirit, or by dissolving it in Alcohol of 805, in which Carbonate, Sulphate, and Iodate are insoluble.

POTASSIUM, SULPHIDE OF.

There are many Sulphides of Potassium, but the one commonly employed by Photographers, and sold in commerce as "Liver of Sulphur," is an impure Ter-

sulphide. It is prepared by heating Sulphur with Carbonate of Potash, the result of which is that a portion of the Sulphur is oxidized into Sulphuric Acid, and combines with Potash, forming Sulphate of Potash, whilst another portion enters into combination with Potassium, producing a Sulphide of Potassium containing three atoms of Sulphur to one of Potassium.

Sulphide of Potassium is used for reducing the Silver from old Hyposulphite of Soda fixing solutions.

POTASSIUM, SULPHOCYANIDE OF.

See SULPHOCYANIDES.

PYROGALLIC ACID.

Formula, $H_3C_6H_3O_3 = 126$.

This substance is obtained by the action of heat of 420° (Fahr.) on Gallic Acid. The acid sublimes and is collected in the form of white shiny scales.

Pyrogallic Acid (sometimes called Pyrogallol) can hardly be called a *real* acid, as it does not redden blue litmus-paper. It is very soluble in water, alcohol, and ether. Its aqueous solution soon decomposes by oxidation; but an Alcoholic or Ethereal solution will remain unchanged for a very long time.

It is a powerful deoxidizer, and reduces the Oxides of all the noble metals, hence its value as a developer in Photography.

PYROXYLIC SPIRIT.

See ALCOHOL, METHYLIC.

PYROXYLINE.

The name Pyroxyline is applied to a series of compounds, obtained by the action of mixed Nitric and Sulphuric Acids on vegetable fibres; they are all more or less explosive, the strongest being Gun Cotton; the soluble varieties are termed sometimes Collodion Wool. They are all *substitution compounds*, being derived from

the vegetable fibre by the *substitution* of atoms of NO_2 for an equal number of atoms of H in the fibre.

Photographic Pyroxyline is prepared with *hot* acids, heat being found remarkably to modify the products, which, *thus* prepared, have not yet been thoroughly analyzed. A mixture of acids which, if *cold*, would give an insoluble cotton, will, when hot, often produce a perfectly soluble product; and another acid mixture which would yield a pyroxyline giving a very viscid *Collodion* with 4 grs. to the ounce, will, when used hot, give a product soluble to the extent of 7 or 8 grs. to the ounce, and yet the solution will be quite fluid.

SEL D'OR. *See* GOLD, HYPOSULPHITE OF.

SILVER.

Symbol, Ag=108.

This metal, the *Luna* or *Diana* of the alchemists, is found native in Peru and Mexico; but its principal ore is the Sulphide.

When pure it has a sp. gr. of 10·5, and is very malleable and ductile; melts at a bright red heat. Silver does not oxidize in the air, but when exposed to an impure atmosphere containing traces of Sulphuretted Hydrogen, it is slowly tarnished, from formation of Sulphide of Silver. It dissolves in strong boiling Sulphuric Acid, but the best solvent for it is Nitric Acid.

The standard coin of the realm is an alloy of Silver and Copper, containing 92·5 per cent. of Silver.

To prepare pure Nitrate of Silver from it, dissolve in Nitric Acid by aid of heat, and evaporate until crystals are obtained. Then wash the crystals with a little dilute Nitric Acid, redissolve them in water, and crystallize by evaporation a second time.

The process is also occasionally conducted by boiling down the impure acid solution of the Silver to dryness,

without any crystallization, and fusing the product pretty *strongly*, until a portion taken out, dissolved in water, and filtered from Oxide of Copper, ceases to give a blue colour with Ammonia, showing that the Nitrate of Copper is quite decomposed; afterwards, recrystallize as before. Perhaps the easiest method is to dissolve the alloy in Nitric Acid, immerse a piece of metallic Copper until the Silver is wholly precipitated, remove the Copper, wash the Silver well with water, then with a little Nitrate of Silver to remove any adhering Copper, and lastly dissolve in Nitric Acid and crystallize; or else take the Silver as precipitated by Copper, wash it and dissolve in Nitric Acid, *avoiding all excess* (or if excess has been added, evaporate carefully to dryness to expel it); and to neutralize and remove traces of Copper, add Oxide of Silver to the boiling solution until on filtering and testing a portion with Ammonia, no blue colour is perceived, then filter the whole. This solution, if of the right strength (*see* Appendix), might be used at once for Photographic purposes.

SILVER, ACETATE OF.

Formula, $AgC_2H_3O_2 = 167$.

This is a difficultly soluble salt, deposited in white lamellar crystals when an Acetate is added to a strong solution of Nitrate of Silver.

It is sometimes used as an addition to the Negative Nitrate Bath, but as the commercial Acetate of Silver is often impure and contaminated with Carbonate of Silver—which would make the Bath alkaline—it is better to use the Acetate of Soda, according to the directions to be given afterwards.

SILVER, ALBUMINATE OF.

This name has been given to the insoluble white substance precipitated on adding Nitrate of Silver to a

solution of Albumen, and which analysis shows to contain Oxide of Silver combined with the animal matter. It is reducible to a red sub-compound, both by white light and by Hydrogen Gas.

SILVER, AMMONIO-NITRATE OF.

Crystallized Nitrate of Silver absorbs Ammoniacal gas rapidly, with production of heat sufficient to fuse the resulting compound, which is white, and contains 22·5 per cent. of Ammonia with 77·5 per cent. of Nitrate of Silver. The solution however which Photographers employ, is prepared by adding to the solution of Nitrate of Silver, *quite neutral*, a pure solution of Ammonia until the precipitate which first forms is *nearly* redissolved, and then filtering.

Ammonio-nitrate of Silver is often used for sensitizing *plain*-salted paper for Positive printing; but it is not suited for Albuminized paper, as the Ammonia dissolves off the Albumen.

SILVER, BROMIDE OF.

AgBr = 188.

This salt is now much used in Photography, especially in the dry processes.

It may be produced, either by direct union of its elements, as in the Daguerreotype process, or by double decomposition between Nitrate of Silver and a soluble Bromide, as in the wet and *emulsion* processes of Photography.

Bromide of Silver is insoluble in water: soluble in alkaline Hyposulphites, Cyanides, Sulphocyanides, and Ammonia. By exposure to light it darkens to a tawny grey colour; yet, like the corresponding Iodide, it is capable of yielding, by development, a visible from an invisible image in the Camera.

SILVER, CARBONATE OF.

Formula, $Ag_2,CO_3 = 276$.

This is a white or yellowish powder deposited on adding any soluble Carbonate to solution of Nitrate of Silver. It is only slightly soluble in water, or in solution of Nitrate of Silver, but yet sufficiently so to produce an alkaline reaction to Litmus. More soluble in water containing Nitrate of Ammonia, and freely so in Ammonia itself. Also dissolved by dilute Nitric or Acetic Acid, forming a Nitrate or Acetate.

SILVER, CHLORIDE OF.

Formula, $AgCl = 143{\cdot}5$.

Chloride of Silver may be obtained by the direct union of Silver and Chlorine, or, as in the preparation of papers for Positive printing, by double decomposition of Nitrate of Silver and an alkaline Chloride.

On mixing the solutions, the Chloride of Silver falls as a curdy white precipitate, insoluble in water and Nitric Acid, very soluble in alkaline Hyposulphites, Cyanides, and Sulphocyanides, and in Ammonia even when dilute. On exposure to light, it goes through various shades of violet until it becomes finally black.

SILVER, CITRATE OF.

Formula, $Ag_3C_6H_5O_7 = 513$.

A white salt precipitated on adding a soluble Citrate to solution of Nitrate of Silver. Its property of being reduced to a coloured subsalt by the action of light, or by a deoxidizing agent, renders it useful in Photography.

Citric Acid added to solution of Nitrate of Silver produces no precipitation. This acid is what is termed tribasic—*i.e.* an acid, *one* atom of which combines with *three* atoms of base to form a neutral Salt.

SILVER, FLUORIDE OF.

Formula, AgF = 127.

This compound differs essentially from the other silver haloids in being *soluble* in water. The dry salt fuses on being heated, and is reduced by a higher temperature, or by exposure to light.

SILVER, HYPOSULPHITE OF.

Formula, $Ag_2S_2O_3 = 328$.

This salt may be obtained by adding a dilute solution of Nitrate of Silver to an excess of concentrated Hyposulphite of Soda; it is thrown down, mixed with a little Sulphide of Silver, from which it is separated after washing by Ammonia, which dissolves the Hyposulphite of Silver, and from which it is precipitated by *exact* neutralization with Nitric Acid.

White, nearly insoluble, and tastes sweet; it is very unstable, easily decomposing into Sulphide of Silver and Sulphuric Acid.

It forms two double salts with Hyposulphite of Soda: one is very soluble in water; the other salt is sparingly soluble. These salts, when in solution, are precipitated by Iodide of Potassium, but not by Chloride of Sodium. They are far more stable than the simple Hyposulphite. Taste, exceedingly sweet.

SILVER, IODIDE OF.

Formula, AgI = 235.

Iodide of Silver in the Daguerreotype process is produced by the direct union of its elements, but in the wet processes of Photography by double decomposition of Nitrate of Silver and a soluble Iodide.

Obtained by mixing solutions of Nitrate of Silver and an alkaline Iodide, it forms a yellow precipitate.

This compound differs from the Chloride and Bromide of Silver in being insoluble in Ammonia, but it resembles them in being soluble in alkaline Hyposulphites, Cyanides, and Sulphocyanides, and to some extent in concentrated solutions of the Alkaline Chlorides, Bromides and Iodides. Heat changes it temporarily to deep yellow. Light turns it brown.

SILVER, NITRATE OF.

Formula, $Ag,NO_3 = 170$.

Preparation and Properties.—The preparation of Nitrate of Silver has been sufficiently described under the head of Silver, to which the reader is referred. There are, however, some points of practical importance yet to be considered.

Pure Nitrate of Silver may be made from alloys of Silver and Copper, as described (art. SILVER); but since the heat which is necessary to decompose the Nitrate of Copper often produces Nitrite of Silver, it is advised that Silver nearly free from Copper should be chosen in preference. The consumption of Nitrate of Silver in Photography has now become very large, and it fortunately happens that the crystallized salt can be obtained in almost any quantity at a moderate price, being a bye-product in the operations of parting Gold and Silver, which are carried on in the refineries. The assay processes also yield a portion of the Nitrate sold in commerce, but not by any means the greater part.

This facility of obtaining commercial crystallized Nitrate of Silver at a price which is very little above that of the metal it contains, has, however, acted injuriously as regards the purity of the article, since it necessarily leaves its manufacture in the hands of a few individuals, who are not able to pay that attention to it which is needed. The crystals are usually sent out simply dried off from the Nitric Acid, as a refuse product on which no profit can be expected. Inten-

tional adulteration, however, is not practised by the large producers of Nitrate of Silver, as far as the Author is aware.

The purity of Nitrate of Silver may easily be ascertained by dissolving a portion in distilled water, and precipitating the solution entirely with pure Hydrochloric Acid; the liquid filtered from the precipitate should leave no residue on evaporation to dryness.

Nitrate of Potash and Nitrate of Copper have been spoken of as occasional impurities in commercial Nitrate of Silver, but the presence of these salts in small quantity would have little effect except in reducing the strength of the Baths. The peculiar Photographic action of bad Nitrate of Silver is probably to be referred to a different cause—viz., to the presence of oxidized organic matter. In the assay processes, fragments of charcoal are introduced to prevent the acid from *bumping* as it dissolves the Silver; we have good reason for believing that, during this process, the Nitric Acid oxidizes the charcoal into a substance which has an affinity for the Silver salt; and the Author has found that Nitrate of Silver so produced is altogether unfit for Collodion Photography.

When the old Nitrate Baths are precipitated by Zinc, organic matter is carried down by the reduced Silver, and the product, if converted into Nitrate of Silver without previous fusion, is useless for Photographic purposes.

Impurities of a similar kind, but in less quantity, have been detected, in cases where no Charcoal had been employed. Pieces of straw, etc., may perhaps fall into the acid; but, however this may be, the fact is certain that Nitrate of Silver prepared by dissolving Silver in Nitric Acid, and evaporating to dryness without any crystallization, cannot be depended on for Photography.

It has been suggested that the Nitrate of Silver for the Bath should be made purposely by dissolving pure Silver in pure Nitric Acid. Probably, however, no

manufacturer would care to compete with the refiners, who are in a better position to supply the article at a reasonable price. *Recrystallization* seems therefore to be the proper remedy. The first crop of crystals may be dried off from the acid, and then crystallized a second time from distilled water; after which the product will be in a pure state if charcoal and substances of that kind have been excluded. This second crystallization ought not, according to a competent authority, to add more than fourpence, or at most sixpence, to the price per ounce.

A saturated solution of the purified crystals slowly restores the blue colour of reddened litmus-paper, if the Nitric Acid be expelled by heating to 240° previous to the second crystallization. This proceeding, however, is not actually necessary, inasmuch as a trace of adhering Nitric Acid can always be removed by Carbonate of Soda when making the Bath; and it is well known that the presence of a little acid facilitates the crystallization of Nitrate of Silver.

SILVER, NITRITE OF.

Formula, $AgNO_2 = 154$.

Nitrite of Silver is a compound of Nitrous Acid, or HNO_2 with Oxide of Silver. It may be formed by heating Nitrate of Silver, so as to drive off a portion of its Oxygen, or by mixing Nitrate of Silver and Nitrate of Potash in equal parts, fusing strongly, and dissolving in a small quantity of boiling water: on cooling, the Nitrite of Silver crystallizes out, and may be purified by pressing blotting-paper; but the best method of producing it is to fuse *pure* Nitrate of Potash (free from chloride) in a crucible, at a strong red-heat, until a portion removed, dissolved in water and tested with Nitrate of Silver, is found to give a *brownish* precipitate due to a portion of free Potash; when this is the case, it is allowed to cool, and 1 part of the product is then dis-

solved in 20 of boiling water and mixed with 2 parts of Nitrate of Silver, also dissolved in 20 of boiling water, mix, filter *rapidly* through a hot filter; on cooling the Nitrite of Silver crystallizes out abundantly from the liquid.

Properties.—Nitrite of Silver is soluble in 120 parts of cold water, easily soluble in boiling water, and crystallizes on cooling, in long slender needles. A small quantity dissolved in the Negative Bath increases the sensitiveness and intensity of the Collodion surface, but it has a tendency to produce fogging.

SILVER, OXIDE OF.

Formula, $Ag_2O = 232$.

Oxide of Silver may be obtained by adding a solution of Potash (pure or nearly free from Chloride) to one of Nitrate of Silver; a brown-black precipitate of Oxide of Silver falls, which may be collected on a filter and washed, or it may be allowed to settle down, the clear liquid poured off, fresh water added, and the Oxide again allowed to settle; this being repeated until the Nitrate of Potash and Potash have been removed, which may be ascertained either by evaporating a little on a slip of glass, or, if excess of Potash was added in the first place, by testing with red litmus-paper. It may be kept in a bottle in a moist state, its use being to neutralize Nitrate of Silver Baths, and to separate Oxide of Copper from Nitrate of Silver; the bottle should be kept in the dark.

SILVER, SULPHIDE OF.

Formula, $Ag_2S = 248$.

This compound, sometimes termed Sulphuret of Silver, is formed by the action of Sulphur upon metallic Silver, or of Sulphuretted Hydrogen or Hydrosulphate of Ammonia upon the Silver salts: the decomposition

of Hyposulphite of Silver also furnishes the black Sulphide.

Sulphide of Silver is insoluble in water, and in those substances which dissolve the Chloride, Bromide, and Iodide, such as Ammonia, Hyposulphites, Cyanides, etc.; but it dissolves in Nitric Acid, being converted into soluble Sulphate and Nitrate of Silver.

The colour of precipitated Sulphide of Silver varies with the quantity present; it is black when in mass, but yellowish-brown in a state of fine division.

SODA, ACETATE OF.

Formula, $Na,C_2H_3O_2 + 3H_2O = 136$.

An easily crystallizable salt, employed commercially as a source of Acetic Acid. There are several qualities, some of which contain brown empyreumatic matter, but the recrystallized salt can usually be obtained pure. It is readily soluble in water, and also in Alcohol.

This Acetate is undoubtedly the best form to employ in Photography, since Acetate of Potash is deliquescent, and cannot easily be kept dry. It is often used along with Chloride of Gold for toning Silver prints.

SODA, CARBONATE OF.

Formula, $Na_2,CO_3 + 10$ Aq. $= 286$.

There are two Carbonates of Soda. The one (Carbonate) is the common washing Soda. The other is the Bicarbonate, which is used in Photography sometimes for neutralizing a too acid Silver bath, and very often in the Chloride of Gold toning bath.

SODA, CITRATE OF.

Formula, $Na_3C_6H_5O_7 = 258$.

This salt, the composition of which is analogous to the Citrate of Silver, *q. v.*, yields well-defined crystals,

but as it is sometimes difficult to obtain it in commerce, instructions are given in this Work for making it extemporaneously by neutralizing 56 grains of pure Citric Acid with 66 grains of dry Sesquicarbonate of Soda, quantities which will yield 95 grains of Citrate of Soda.

The crystals are very soluble in water, and produce a white flocculent deposit of Citrate of Silver in solution of Nitrate of Silver.

SODA, HYPOSULPHITE OF,

Formula, $Na_2S_2O_3 + 5Aq = 248$,

is a salt largely used in Photography for fixing images. This it effects by virtue of the power which it possesses of dissolving the Haloid salts of Silver. This property was discovered many years ago by Sir John Herschel.

Hyposulphite of Soda is made on an extensive scale, mainly for the purposes of the paper manufacturers, who employ it as an *antichlor*, or absorbent of the Chlorine used in bleaching the pulp of linen and cotton rags. Some of the inferior qualities have a yellowish colour, arising probably from Sulphide or free Sulphur. This kind should not be used for a fixing solution, as it is sure to impregnate the print with that deadly enemy to silver photographs—Sulphur. Acids, even in minute quantity, decompose it, liberating Sulphur. Hence the importance of keeping Hyposulphite solutions in a slightly alkaline, or at least neutral, state.

SODA, PHOSPHATE OF.

Formula, $Na_2HPO_4 + 12H_2O = 358$.

There are several Phosphates of Soda, but the common Phosphate has the above composition. It forms large transparent crystals which effloresce, and become opaque on the exterior; soluble in four parts of cold

water, the solution possessing a faint alkaline reaction; precipitates Nitrate of Silver yellow.

Pyrophosphate of Soda, so called, is prepared by heating the ordinary Phosphate until the whole of the water has been expelled; when the residue is dissolved in water it is found to have been completely altered in properties, as it precipitates Nitrate of Silver white instead of yellow; it crystallizes in prisms. Formula, $2Na,PO_3$.

SODIUM, AURO-CHLORIDE OF.

Formula, $NaCl,AuCl_3 + 4Aq = 397{\cdot}6$.

This salt is a double Chloride of Gold and Sodium, with four atoms of water of crystallization. It has been proposed as a convenient substitute for the ordinary Chloride of Gold, as it is not deliquescent, and forms long orange-yellow, four-sided prisms. Another advantage is the absence of free acid in the double salt, whereas the ordinary Chloride of Gold always contains Hydrochloric Acid. The Auro-Chloride however will not in all probability come into general use in Photography, since it is evidently open to adulteration, and although theoretically neutral, yet the manfacturers themselves allow that it will not be safe to calculate upon perfect neutrality, since traces of Hydrochloric Acid are apt to remain in the interstices of the crystals.

It is prepared by evaporating to dryness a solution of 4 of Gold in Aqua Regia, dissolving the residue in water, adding 1 part of common salt, evaporating the whole down to 4 parts and leaving it to crystallize by cooling.

The pure salt contains 49·7 per cent. of Gold. The amount of Gold may be ascertained by taking a given weight of the compound, dissolving it in water, and boiling it with half its weight of Oxalic Acid; the whole of the Gold separates in the metallic state, and may then be washed, dried, and weighed. The Gold

may also be separated by the addition of five times the weight of Sulphate of Iron, according to directions under GOLD, CHLORIDE OF.

SODIUM, CHLORIDE OF.

Formula, $NaCl = 58{\cdot}5$.

Common Salt exists abundantly in Nature, both in the form of solid rock-salt, and dissolved in the waters of the ocean.

Properties.—Fusible without decomposition at low redness, but sublimes at higher temperatures; the melted salt concretes into a hard white mass on cooling. Nearly insoluble in absolute Alcohol, but dissolves in minute quantity in rectified spirit. Soluble in three parts of water, both hot and cold. Crystallizes in cubes, which are anhydrous.

Impurities of Common Salt.—Table Salt usually contains some Chloride of Magnesium, which, being deliquescent, produces a dampness by absorption of atmospheric moisture: Sulphate of Soda is also commonly present. The salt may be purified by repeated recrystallization, but it is more simple to prepare the pure compound *directly*, by neutralizing Hydrochloric Acid with Carbonate of Soda.

SODA, SULPHITE OF.

Formula, $Na_2SO_3 = 126$.

This salt, which has recently been introduced into the photographic laboratory for the special purpose of preserving aqueous solutions of Pyrogallol, is formed by passing a stream of Sulphurous Acid gas through a concentrated solution of Carbonate of Soda to saturation. It forms large regular crystals, which are soluble in three parts of water at the normal temperature. The soluble metallic Sulphites possess powerful bleaching properties, and their strong affinity for Oxygen,

by which they are converted into Sulphates, renders them valuable for the prevention of oxidation of such substances as Pyrogallol.

SULPHOCYANIDES.

Solutions of the Sulphocyanides of Ammonium or Potassium have been recommended for fixing positive photographs, instead of Hyposulphite of Soda. But it is doubtful whether any advantage is gained.

SULPHURETTED HYDROGEN.

See HYDROSULPHURIC ACID.

SULPHURIC ACID.

Formula, $H_2SO_4 = 98$.

Sulphuric Acid is the highest Oxide of Sulphur; the liquid acid, when most concentrated, always has 1 atom of water, H_2O,SO_3 or H_2SO_4. The commercial process for the manufacture of Sulphuric Acid is exceedingly ingenious and beautiful, but it involves many complicated reactions. The Sulphur is first burnt into gaseous Sulphurous Acid, SO_2, and then, in the presence of vapour of water, by the agency of Binoxide of Nitrogen gas, an additional atom of Oxygen is conveyed to the SO_2, converting it into H_2SO_4, or Sulphuric Acid.

Properties.—Anhydrous Sulphuric Acid is a white crystalline solid. The strongest liquid acid always contains one atom of water, which is chemically combined with it, and cannot be driven off by the application of heat.

This *monohydrated* Sulphuric Acid, represented by the formula H_2SO_4, is a dense fluid, having a specific gravity of about 1·845; boils at 620°, and distils without decomposition. It is not volatile at common temperatures, and therefore does not *fume* like Nitric or

Hydrochloric Acid. The concentrated acid may be cooled down, even to zero, without solidifying; but a weaker compound, containing twice the quantity of water, and termed *glacial* Sulphuric Acid, crystallizes at 40° Fahr. Sulphuric Acid is intensely acid and caustic, but it does not destroy the skin or dissolve metals so readily as Nitric Acid. It has an energetic attraction for water, and when the two are mixed, condensation ensues, and much heat is evolved; four parts of acid and one of water produce a temperature equal to that of boiling water. Mixed with Nitric Acid and a certain proportion of water, it forms the liquid called by Photographers Nitro-Sulphuric Acid.

Sulphuric Acid possesses intense chemical powers, and displaces the greater number of ordinary acids from their salts. It *chars* organic substances, by removing the elements of water, and converts Alcohol into Ether in a similar manner. The *strength* of a given sample of Sulphuric Acid may be calculated, nearly, from its specific gravity, and a Table is given by Dr. Ure for that purpose. (See Appendix.) It is quite necessary, however, that the temperature should be attended to in taking the specific gravity, since a few degrees higher or lower than the point mentioned cause a considerable difference.

Impurities of Commercial Sulphuric Acid.—The liquid acid sold as *Oil of Vitriol* is tolerably constant in composition, and seems to be as well adapted for Photographic use as the *pure* Sulphuric Acid, which is far more expensive. The specific gravity is often about 1·836 at 60°, but an acid of 1·843 or 1·845 at 60° Fahr. can always be obtained of the manufacturers, and is preferable for employment in Photography. If a drop, evaporated upon Platinum foil, gives a fixed residue, probably Bisulphate of Potash is present. A milkiness, on dilution, indicates Sulphate of Lead; a little Sulphate of Lead, however, would not interfere, and may be disregarded. Commercial Sulphuric Acid sometimes bleaches Sulphate of Indigo, on boiling a

diluted solution: this is due to traces of Nitric Acid present in the Oil of Vitriol.

Test for Sulphuric Acid.—If the presence of Sulphuric Acid, or a soluble Sulphate, be suspected in any liquid, it may be tested for by adding a few drops of dilute solution of Chloride of Barium, or of Nitrate of Baryta. A white precipitate, *insoluble in Nitric Acid*, indicates Sulphuric Acid. If the liquid to be tested is very acid, from Nitric or Hydrochloric Acid, it must be largely diluted before testing, or a crystalline precipitate will form, caused by the sparing solubility of the Chloride of Barium itself in acid solutions.

TANNIN.

Formula, $C_{14}H_{10}O_9 = 322$.

Various organic substances, possessing an astringent action, have been termed "Tannin;" such, for instance, as the extractive matters from bark, used in tanning hides, the astringent principles of Tea and Coffee, etc. The most important, however, is the Tannin of the Gall Nut, known as "Tannic Acid," or "Gallo-Tannic Acid."

Gall Nuts contain as much as two-thirds of their weight of Tannic Acid, which is extracted by reducing the nuts to powder, and digesting them with washed Ether: the decanted liquid separates on standing into two portions, the lower being an aqueous solution of Tannic Acid, the watery constituent of which is derived from the *washed* Ether (*see* ETHER). On evaporating the aqueous solution to dryness, a porous, buff-coloured residue of Amorphous Tannic Acid is obtained.

Tannic Acid is freely soluble in water, but it rarely yields a clear solution, on account of traces of remaining resinous matter. The reaction to test-paper is slightly acid, and on adding an alkali a "Tannate" is formed, but the alkaline Tannates are very unstable, and tend to absorb Oxygen and become brown. Tannic

Acid gives with the Persalts of Iron a violet-black precipitate, which is the basis of common Writing Ink. Solutions of Gelatine are precipitated by Tannic Acid in the form of Tanno-Gelatine, the material of Leather: Albumen is also coagulated by Tannin. When Tannic Acid is heated to about 600° Fahr., it is decomposed, and yields Pyrogallic Acid. Nitrate of Silver is not precipitated by Tannic Acid, but suffers a slow reduction to the state of Metallic Silver.

TARTARIC ACID.

Formula, $C_4H_6O_6 = 150$.

This Acid is derived from a substance called *Tartar*, deposited from the juice of the Grape during fermentation. This Tartar is an Acid Tartrate of Potash, and purified by crystallization and deprived of its base it furnishes this Acid. Tartaric Acid forms colourless, transparent, rhombic prisms, very soluble in Water and Alcohol; it is a bibasic acid. It is used for most purposes in Photography for which Citric Acid is employed.

TETRATHIONIC ACID.

Formula, $S_4O_5 = 104$.

This acid is one of the Oxides of Sulphur, belonging to the interesting series designated by Berzelius the "Polythionic Acids." The composition of this series may be represented as follows :—

	Formulæ.
Dithionic Acid . . .	$H_2S_2O_6$.
Trithionic Acid . . .	$H_2S_3O_6$.
Tetrathionic Acid . .	$H_2S_4O_6$.
Pentathionic Acid . .	$H_2S_5O_6$.

The amount of *Oxygen* in all is the same, that of the other element increases progressively; hence the highest member of the series might *by losing Sulphur*

descend gradually until it reached the condition of the lowest.

Such a transition is not only theoretically possible, but there is an actual tendency to it, all the acids being unstable with the exception of the Dithionic. The Alkaline Salts of these acids are more unstable than the acids themselves; a solution of Tetrathionate of Soda becomes milky in the course of a few days from deposition of Sulphur, and, if tested, is then found to contain *Tri*thionate and eventually *Di*thionate of Soda.

The presence of Hyposulphite of Soda increases the instability of Tetrathionate of Soda. A solution of the latter may be preserved for many hours unchanged, but if a few crystals of Hyposulphite of Soda be dropped in, it begins very shortly to deposit Sulphur, and continues to do so for several days. At the same time the liquid acquires *an acid reaction* to test-paper, and produces effervescence on the addition of Carbonate of Lime.

Tetrathionate of Soda may be formed by acting on Hyposulphite of Soda with Iodine; a colourless solution is obtained, which, in addition to the new salt, contains Iodide of Sodium. Perchloride of Iron, Chloride of Copper, and Chloride of Gold, decompose Hyposulphite of Soda and form Tetrathionate, amongst other products. Acids in a free state have often the same effect, since they liberate Sulphurous Acid, which, in contact with Hyposulphite of Soda, forms Trithionate and Tetrathionate of Soda.

TURMERIC.

Turmeric is the rhizome of an Indian plant. It possesses a yellow colouring matter, curcumin, soluble in Ether and Alcohol. Paper brushed with a strong decoction of Turmeric is used by the Chemist as a test for alkalinity; free alkalies or alkaline bases change the colour from yellow to brown. It is not so sensitive as reddened Litmus, but is useful as indicating a *strong* alkaline reaction.

URANIUM, NITRATE OF.

$(UrO_2),(NO_3)_2 + 6Aq = 384.$

This salt is obtained by dissolving one of the higher oxides of Uranium in Nitric Acid, and evaporating over a water bath.

The remarkable Photographic properties of some of the Uranium salts were first discovered by Mr. Burnett, of Edinburgh. Since then the Nitrate of Uranium has been used conjoined with Silver or Gold in several processes.

The rationale seems to be this. The Uranium *per-salt* is reduced by light to a *proto-salt*, which, when the exposed paper or film is brought in contact with Gold or Silver solutions, reduces them by again absorbing Oxygen and passing into a per-salt.

WATER.

Formula, $H_2O = 18.$

Water is an Oxide of Hydrogen, containing single atoms of each of the gases.

Distilled water is water which has been vaporized and again condensed; by this means it is freed from earthy and saline impurities, which, not being volatile, are left in the body of the retort. *Pure* distilled water leaves no residue on evaporation, and should remain perfectly clear on the addition of Nitrate of Silver, *even when exposed to the light;* it should also be neutral to test-paper.

The condensed water of steam-boilers, often sold in provincial towns and elsewhere as distilled water, is apt to be contaminated with oily and empyreumatic matter, which discolours Nitrate of Silver, and is therefore injurious. Newly-made metal stills also fail at first in giving a pure product, from the presence of grease or dust in the soldered joints. Professor Tomlinson has shown that a very minute amount of grease on water may be

detected by Camphor, which, thrown on water free from grease, rapidly spins round, until it has dissolved or has evaporated, but this motion is prevented by a trace of fatty matter.

Rain-water, having undergone a natural process of distillization, is free from inorganic salts, but it usually contains a minute portion of *Ammonia*, which gives it an alkaline reaction to test-paper. It is very good for Photographic purposes if collected in clean vessels, but when taken from a common rain-water tank should always be examined, and if much organic matter be present, tinging it of a brown colour, and gradually reducing Nitrate of Silver in presence of light, it must be rejected.

Spring or *River* water, commonly known as "hard water," usually contains Sulphate of Lime, and Carbonate of Lime dissolved in Carbonic Acid; also Chloride of Sodium in greater or less quantity. On boiling the water for twenty minutes or half an hour, the Carbonic Acid gas is evolved, and the greater part of the Carbonate of Lime (if any be present) deposits, forming an incrustation, which dissolves in Acetic Acid with effervescence. Spring-water is less likely to contain brown organic matter than rain-water.

In testing water for Carbonates, Sulphates, and Chlorides, divide it into two parts, and add to the first a dilute solution of Chloride of Barium, and to the second, Nitrate of Silver*—a milkiness indicates the presence of either Carbonate or Sulphate in the first case, or of Carbonate or Chloride in the second. Next, acidify the two liquids with a few drops of Glacial Acetic Acid: if the opalescence disappears and the fluid becomes clear, Carbonates are present; but if, as is more frequently the case, the cloudiness is only partially removed by the Acetic Acid, then the Carbonate is mixed with Sulphate or Chloride as the case may be.

* The *Photographic Nitrate Bath* cannot be used as a test, since the Iodide of Silver it contains is precipitated on dilution, giving a milkiness which might be mistaken for Chloride of Silver.

Water for the Nitrate Bath.—Common hard water can often be used for making a Nitrate Bath when nothing better is at hand. The Chlorides it contains are precipitated by the Nitrate of Silver, leaving small quantities of soluble *Nitrates* in solution, which are not injurious. Carbonate of Lime, if present, neutralizes acid, and may render the Bath alkaline if Salts of Ammonia are present. Sulphate of Lime causes no precipitation, and ought not theoretically to produce any injurious effect. It has, however, been spoken against by some, but whether from practical experience or not the Writer is uninformed. Organic matter will almost certainly be injurious to the Bath, and therefore, unless the purity of the rain-water can be guaranteed, spring-water will be preferable.

Water for the Developing Solutions.—Carbonate of Lime in a water ought not to unfit it for the developing liquid in presence of free Acetic Acid, because the chalk would be decomposed under such circumstances, and converted into Acetate of Lime, which would probably assist a little in increasing the intensity. In the case of Sulphate of Iron, chalky water throws down a small quantity of Oxide of Iron, which produces turbidity and a rusty colour at the edges of the pictures; but any acid added to the developer dissolves it and renders the liquid again clear. Chalk in water used for the Gallic Acid developer, makes it discolour quickly with Nitrate of Silver, but a minim of Acetic Acid to each two ounces is a remedy, as before shown.

Soluble Chlorides are always injurious in water used for developing, because they decompose the Nitrate of Silver on the film, producing a curdy precipitate and lessening the available strength. Acids have no effect in removing Chlorides, but they may be separated by shaking up the water with a graduated quantity of Nitrate of Silver, and filtering it. In this process, however, there is always a difficulty in knowing how much of the Nitrate will be needed, since the least excess over the quantity required to decomposed the salt

causes the water to blacken on adding Pyrogallic Acid. This might be obviated, however, by keeping the Pyrogallic Acid dissolved in Glacial Acetic Acid, and adding the water only when required. Bear in mind also that it will not be necessary to remove every trace of salt from the water, since it is quite possible to bring out a perfect image with a developing solution which produces a decided turbidity on first touching the film: especially so if a few drops of solution of Nitrate of Silver be added to the developer immediately before use.

CHAPTER III.

THE SALTS OF SILVER EMPLOYED IN PHOTOGRAPHY.

By the term *Salt* of Silver we understand that the compound in question contains Silver, but not in its elementary form; the metal is in fact in a state of chemical union with other elements which disguise its physical properties, so that the salt possesses none of the external characters of the Silver from which it was produced.

The contents of this Chapter may be arranged in three Sections: the first describing the Chemistry of the Salts of Silver; the second, the action of Light upon them; the third, the preparation of a sensitive surface, with experiments illustrating the formation of the Photographic image.

SECTION I.

Chemistry of the Salts of Silver.

The principal Salts of Silver employed in the Photographic processes are four in number—viz., Nitrate of Silver, Chloride of Silver, Iodide of Silver, and Bromide of Silver. In addition to these it will be necessary to describe the Oxides of Silver.

THE PREPARATION AND PROPERTIES OF THE NITRATE OF SILVER.

Nitrate of Silver is prepared by dissolving metallic Silver in Nitric Acid. Nitric Acid is a powerfully acid and corrosive substance, containing two elementary bodies united in definite proportions: these are Nitro-

gen and Oxygen; the latter being present in greatest quantity.

Nitric Acid is a powerful solvent for the metallic bodies generally. To illustrate its action in that particular, as contrasted with other acids, place pieces of silver-foil in two test-tubes, the one containing dilute Sulphuric, the other dilute Nitric Acid; on the application of heat a violent action soon commences in the latter, but the former is unaffected. In order to understand this, it must be borne in mind that when a metallic substance dissolves in an acid, the nature of the solution is different from that of an aqueous solution of salt or sugar. If salt water be boiled down until the whole of the water has evaporated, the salt is recovered with properties the same as at first; but if a similar experiment be made with a solution of Silver in Nitric Acid, the result is different: in that case we do not obtain *metallic* silver on evaporation, but Silver *combined with Oxygen and Nitric Acid*, both of which are in a state of chemical combination with the metal.

Properties of Nitrate of Silver.—In preparing Nitrate of Silver, when the metal is dissolved, the solution is boiled down and set aside to crystallize. The salt however so obtained is still acid to test-paper, and requires either recrystallization, or careful heating to about 300° Fahrenheit. It is this retention of small quantities of Nitric Acid, and other impurities, which renders much of the commercial Nitrate of Silver useless for Photography, until after a second crystallization.

Pure Nitrate of Silver occurs in the form of white crystalline plates, which are very heavy, and dissolve readily in an equal weight of cold water. The solubility is much lessened by the presence of free Nitric Acid, and in the *concentrated* Nitric Acid the crystals are almost insoluble. Boiling Alcohol takes up about one-fourth part of its weight of the crystallized Nitrate, but deposits nearly the whole on cooling. Nitrate of Silver has an intensely bitter and nauseous taste;

acting as a caustic, and corroding the skin by prolonged application. Its aqueous solution does not redden blue litmus-paper: on the contrary, the pure recrystallized and dried Nitrate of Silver restores the blue colour of paper previously reddened.

Heated in a crucible the salt melts, and when poured into a mould and solidified, forms the white *lunar caustic* of commerce. At a still higher temperature it is decomposed, and bubbles of Oxygen gas are evolved: the melted mass cooled and dissolved in water yields a solution, which contains Nitrite in addition to Nitrate of Silver.*

THE CHEMISTRY OF THE CHLORIDES OF SILVER.

Preparation of Chloride of Silver (AgCl).—The ordinary white Chloride of Silver may be prepared in two ways—by the direct action of Chlorine upon metallic Silver, and by double decomposition between two salts.

If a plate of polished silver be exposed to a current of Chlorine gas, it becomes, after a short time, coated on the surface with a superficial film of white powder. This powder is Chloride of Silver, containing the two elements, Chlorine and Silver, united in single equivalents.

Preparation of Chloride of Silver by double decomposition.—In order to illustrate this, take a solution in water of Chloride of Sodium, or "common salt," and mix it with a solution containing Nitrate of Silver; immediately a dense, curdy, white precipitate falls, which is the substance in question.

In this reaction the elements change places; the Chlorine leaves the Sodium with which it was previously combined, and crosses over to the Silver; the Nitric Acid is released from the Silver, and unites with the Sodium; thus

$$NaCl + Ag,NO_3 = Na,NO_3 + AgCl.$$

* Nitrite of Silver differs from the Nitrate in containing less Oxygen, and is formed from it by the abstraction of two atoms of that element; it is described in the Vocabulary.

This interchange of elements is an example of *double decomposition.*

In preparing Chloride of Silver by double decomposition, the white clotty masses which first form must be washed repeatedly with water, in order to free them from soluble Nitrate of Soda, the other product of the change. When this is done, the salt is in a pure state, and may be dried, etc., in the usual way.

Properties of Chloride of Silver.—Chloride of Silver forms a soft white powder resembling common chalk or whiting. It is tasteless and insoluble in water: unaffected by boiling with the strongest Nitric Acid, but sparingly dissolved by concentrated Hydrochloric Acid.

Ammonia dissolves Chloride of Silver freely, as do solutions of Hyposulphite of Soda and Cyanide of Potassium. Concentrated solutions of the Sulphocyanide, Chloride, Iodide, and Bromide of Potassium, Sodium, and Ammonium, are likewise solvents of Chloride of Silver, but to a limited extent.

Dry Chloride of Silver carefully heated to redness fuses, and concretes on cooling into a tough and semi-transparent substance, which has been termed *horn silver* or *luna cornea.*

Placed in contact with metallic Zinc or Iron acidified with dilute Sulphuric Acid, Chloride of Silver is reduced to the metallic state, the Chlorine passing to the other metal under the decomposing influence of the galvanic current which is established.

$$2AgCl + Zn = ZnCl_2 + 2Ag.$$

Preparation and Properties of Subchloride of Silver.—If a plate of polished Silver be dipped into a solution of Perchloride of Iron, a *black stain* is produced, the Perchloride sinking to the state of a *Proto*-chloride of Iron, and losing a portion of Chlorine, which passes to the Silver and converts it superficially into a Subchloride of Silver.

This compound differs from the white Chloride of

Silver in containing less Chlorine. As it has not been obtained sufficiently pure for analysis, no formula can be assigned to it. The only facts certainly ascertained with regard to the Subchloride of Silver are, that it is a pulverulent substance of a bluish-black colour, not easily affected by Nitric Acid, but decomposed by fixing agents, such as Ammonia, Hyposulphite of Soda, or Cyanide of Potassium, into Chloride of Silver, which dissolves, and insoluble metallic Silver.

THE CHEMISTRY OF IODIDE OF SILVER.

The properties of *Iodine* are described in the first Part of the Work; they are analogous to those of Chlorine and Bromine, the Silver Salts formed by these elements bearing also a strong resemblance to each other.

Preparation and Properties of Iodide of Silver (AgI). —Iodide of Silver may be formed in an analogous manner to the Chloride—viz., by the direct action of the vapour of Iodine upon metallic Silver, or by double decomposition between solutions of Iodide of Potassium and Nitrate of Silver.

When prepared by the latter mode it forms an impalpable powder, the colour of which varies with the manner of precipitation. If the Iodide of Potassium be in excess, the Iodide of Silver, nearly white, falls to the bottom of the vessel; but with an excess of Nitrate of Silver it is of a straw-yellow tint. This point may be noticed, because the yellow condition is the one adapted for Photographic use, the other being insensible to the influence of Light.

Iodide of Silver is tasteless and inodorous; insoluble in water and in dilute Nitric Acid. It is scarcely dissolved by Ammonia, which serves to distinguish it from the Chloride of Silver, freely soluble in that liquid. Hyposulphite of Soda and Cyanide of Potassium both dissolve Iodide of Silver; it is also soluble in solutions of Sulphocyanide, Bromide, and Iodide of Potassium,

Sodium, and Ammonium, as will be further explained in Chapter V.

Iodide of Silver is reduced by Metallic Zinc in the same manner as the Chloride of Silver, forming soluble Iodide of Zinc and leaving a black powder of metallic Silver.

$$2AgI + Zn = ZnI_2 + 2Ag.$$

THE PREPARATION AND PROPERTIES OF BROMIDE OF SILVER.

This substance so closely resembles the corresponding salts containing Chlorine and Iodine, that a short notice of it will suffice.

Bromide of Silver (AgBr) is prepared by exposing a silvered plate to the vapour of Bromine, or by adding solution of Bromide of Potassium to Nitrate of Silver. It is insoluble in water, slightly yellow in colour, and distinguished from Iodide of Silver by dissolving in strong Ammonia and in Chloride of Ammonium. It is freely soluble in Hyposulphite of Soda and in Cyanide of Potassium.

CHEMISTRY OF THE OXIDES OF SILVER.

The Protoxide of Silver (Ag_2O).—If a little Potash or Ammonia be added to solution of Nitrate of Silver, an olive-brown substance is formed, which, on standing, collects at the bottom of the vessel. This is Oxide of Silver, displaced from its previous state of combination with Nitric Acid by the stronger oxide, Potash. Oxide of Silver is soluble *to a very minute extent* in pure water, the solution possessing an alkaline reaction to Litmus; it is easily dissolved by Nitric or Acetic Acid, forming a neutral Nitrate or Acetate of Silver; it also dissolves in Ammonia (Ammonio-Nitrate of Silver), Nitrate of Ammonia, Hyposulphite of Soda, and Cyanide of Potassium.

The Suboxide of Silver (Ag_4O ?).—This compound is distinguished from the Protoxide by the action of Hydrochloric Acid, which, with the latter, produces the

white Chloride, but with the latter the *dark* Subchloride. It has probably never been obtained pure, but a certain amount is obtained, mixed however with Silver and Protoxide, on boiling Arsenite of Silver, $3Ag,AsO_3$, with a solution of Potash: a black powder results, which is the above mixture. On treating this powder, after washing, with Hydrochloric Acid, a mixture of Chloride, Subchloride, and metallic Silver is produced, from which, after washing, the latter may be dissolved out by Nitric Acid, leaving the dark mixture of Chlorides.

SECTION II.

On the Photographic Properties of the Salts of Silver.

In addition to the Salts of Silver described in the First Section of this Chapter there are many others well known to chemists, as the Acetate of Silver, the Sulphate, the Citrate of Silver, etc. Some occur in crystals which are soluble in water, whilst others are pulverulent and insoluble.

The Salts of Silver formed by colourless Acids are white when first prepared, and remain so if kept in a dark place; but they possess the remarkable peculiarity of being darkened by exposure to Light, either alone or in contact with organic substances.

Action of Light upon the Nitrate of Silver.—The Nitrate of Silver is one of the most permanent of the Silver Salts. It may be preserved unchanged in the crystalline form, or in solution in distilled water, for an indefinite length of time, even when constantly exposed to the light of day.

Nitrate of Silver may, however, be rendered susceptible to the influence of Light, by adding to its solution *organic matter*, vegetable or animal. The phenomena produced in this case are well illustrated by dipping a sheet of white paper in a solution of Nitrate of Silver, and exposing it to the direct rays of the sun; it

slowly darkens, until it becomes nearly black. The stains upon the skin produced by handling Nitrate of Silver are caused in the same way, and are seen most evidently when the part has been exposed to light.

The varieties of organic matter which especially facilitate the blackening of Nitrate of Silver are such as tend *to absorb Oxygen;* hence pure vegetable fibre, free from Chlorides, such, for instance, as the Swedish filtering-paper, is not rendered very sensitive by being simply brushed with solution of the Nitrate, but a little grape sugar added soon determines the decomposition.

Decomposition of Chloride, Bromide, and Iodide of Silver by Light.—Pure Chloride of Silver prepared in the moist way changes slowly from white to *violet* on exposure to light. Bromide of Silver becomes of a grey colour, but is less affected than the Chloride. Iodide of Silver (if free from excess of Nitrate of Silver) does not alter in appearance by exposure even to the sun's rays, but retains its yellow tint unchanged. Of these three compounds therefore, *Chloride* of Silver is the most visibly acted on by light, and papers prepared with this salt will become far darker on exposure, than others coated with Bromide or Iodide of Silver.

There are certain conditions which render the action of light upon the Chloride of Silver more decided. These are, first, *an excess of a soluble salt of Silver such as the Nitrate*, and second, *the presence of organic matter.* Pure Chloride of Silver would be useless as a Photographic agent, but a Chloride with excess of Nitrate takes a strong impression. Even Iodide of Silver, ordinarily unaffected, is blackened by light when moistened with a solution of the Nitrate of Silver.

Organic matter combined with Chloride and Nitrate of Silver gives a still higher degree of darkening in the solar ray, and in this way the Photographic papers are prepared.

Action of Light upon Organic Compounds of Silver.—On adding diluted Albumen, or white of egg, to solu-

tion of Nitrate of Silver, a flocculent deposit forms, which is a compound of the animal matter with Oxide of Silver, and is known as "Albuminate of Silver." This substance is at first white, but on exposure to light it assumes a brick-red colour.

Caseine, the animal principle of milk, is coagulated by Nitrate of Silver, the product behaving in the same manner as the Albuminate when exposed to light. Gelatine does not precipitate Nitrate of Silver · but if a sheet of transparent Gelatine be allowed to imbibe a solution of the Nitrate, it combines with it, and the product becomes of a clear ruby-red tint on exposure to light.

Many other organic compounds of Silver are darkened by light. The white Citrate of Silver changes to a red colour. Glycyrrhizine, the Sugar of Liquorice, also forms a white compound with Oxide of Silver, which becomes brown or red in the sun's rays.

The photographic use of the organic Salts of Silver, and the extent to which they are affected by light, will be further considered in the Eighth Chapter, when speaking of the theory of Positive printing.

SIMPLE EXPERIMENTS ILLUSTRATING THE ACTION OF LIGHT UPON A SENSITIVE LAYER OF CHLORIDE OF SILVER ON PAPER.

In the performance of the most simple experiments on the decomposition of Silver Salts by Light, the student may employ ordinary *test-tubes*, in which small quantities of the two liquids required for the double decomposition may be mixed together.

When however *concentrated* solutions are used in this way, the insoluble Silver Salt falls in dense and clotted masses, which, exposed to the sun's rays, quickly blacken on the exterior, but the inside is protected, and remains white. It is of importance therefore in Photography that the sensitive material should exist in the form of *a surface*, in order that the various particles

of which it is composed may each one individually be brought into relation with the disturbing force.

Full directions for the preparation of sensitive Photographic paper are given in another portion of this work. The following is the theory of the process:—A sheet of paper is treated with solution of Chloride of Sodium or Ammonium, and subsequently with Nitrate of Silver; hence results a formation of Chloride of Silver in a fine state of division, with an excess of Nitrate of Silver, since the Silver bath is applied *after* the salting solution, and is made purposely of a greater strength.

Illustrative Experiment No. I.—Place a square of sensitive paper, prepared as above, in the direct rays of the sun, and observe the gradual process of darkening which takes place; the surface passes through a variety of changes in colour until it becomes of a deep chocolate brown. If the Light is tolerably intense, the brown shades are probably reached in from three to five minutes; but the sensibility of the paper, and also the nature of the tints, will vary much with the character of the organic matter present.

Experiment No. II.—Lay a device cut from black paper upon a sheet of sensitive paper, and compress the two together by means of a sheet of glass. After a proper length of exposure the figure will be exactly copied with the tint reversed; the black paper protecting the sensitive Chloride beneath, produces a *white* figure upon a dark ground.

Experiment No. III.—Repeat the last experiment, substituting a piece of lace or gauze-wire for the paper device. This is intended to show the minuteness with which objects can be copied, since the smallest filament will be distinctly represented.

Experiment No. IV.—Take an engraving in which the contrast of light and shade is tolerably well marked, and having laid it closely in contact with the sensitive paper, expose as before. This experiment shows that

the surface darkens in degrees proportionate to the intensity of the light, so that the *half* shadows of the engraving are accurately maintained, and a pleasing gradation of tone is produced.

In the darkening of Photographic papers, the action of the light is quite superficial, and although the black colour may be intense, yet the amount of reduced Silver which forms it is so small that it cannot be conveniently estimated by chemical reagents. This is well shown by the results of an analysis performed by the Author, in which the total weight of Silver obtained from the blackened sheet measuring nearly 24 by 18 inches, amounted to less than *half a grain*. It becomes therefore of great importance in preparing sensitive paper, to attend to the condition of the surface layer of particles, the action rarely extending to those beneath. The use of Albumen, Gelatine, etc., which will be explained subsequently, has reference to this amongst other advantages, and secures a better and more sharply defined print.

THE NATURE OF THE CHEMICAL CHANGES PRODUCED BY LIGHT UPON COMPOUNDS OF SILVER.

Action of Light upon Chloride of Silver.—This may be studied by suspending pure Chloride of Silver in distilled water, and exposing it to the sun's rays for several days. When the process of darkening has proceeded to some extent, the supernatant liquid will be found to contain *free Chlorine*.

The luminous rays appear to loosen the affinity of the elements Chlorine and Silver for each other; hence a portion of Chlorine is separated, and the white Protochloride is converted into a violet *Sub*chloride of Silver. If an atom of Nitrate of Silver be present, the liberated Chlorine unites with it, displacing Nitric Acid, and forming again Chloride of Silver, which is decomposed in its turn. The excess of Nitrate of Silver thus assists the darkening of Chloride of Silver,

by rendering the chain of chemical affinities more complete, and preventing an accumulation of Chlorine in the liquid.

The violet-coloured compound, the product of the darkening action of light, has been spoken of by some writers as a mixture of Chloride of Silver and Metallic Silver, but the fact that white Chloride of Silver will darken in the sun's rays, even when covered with strong Nitric Acid, proves that the colour is not due to metallic Silver, but to a Subchloride.

The properties of this Subchloride are as follows:— It is very little affected by Nitric Acid, but quickly acted on by those bodies which Photographers employ as fixing agents—viz., Ammonia, Hyposulphite of Soda, and Cyanide of Potassium; the greater part being dissolved by the fixing agent, and a minute portion of Metallic Silver remaining insoluble.

Chemical Changes in Organic Salts of Silver.— White Albuminate of Silver is soluble in Ammonia, and also in Hyposulphite of Soda; but after having been reddened by exposure to light, very little effect is produced upon it by these fixing agents. Gelatine saturated with Nitrate of Silver and exposed to light, loses its characteristic property of dissolving in hot water, but when treated with boiling solution of Potash, it is taken up, forming a clear liquid of a blood-red colour.

From these facts, and others not mentioned, we infer that in the action of light upon Organic Salts of Silver, the Oxide of Silver loses Oxygen, and sinks to the state of a Suboxide, just as Chloride of Silver parts with a portion of Chlorine when exposed to light, and becomes a Subchloride. The organic body is probably oxidized, and the products are left in combination with each other. The present state of our knowledge will not allow of more than a general indication of the nature of these changes; no exact formulæ can be given.

Nature of the Blackening of Photographic Papers.— In this case both Chloride of Silver and Nitrate of

Silver are present, supported by an organic basis. To ascertain the nature of the darkening action of light upon a surface of this kind, it is better to spread the Chloride upon a glass plate, and to make two experiments, adding organic matter in one, and omitting it in the other. Chloride of Silver does not readily adhere to glass unless the surface of the glass be finely ground, and even then very careful manipulation is required. A more simple plan is to employ *Collodion* as a vehicle for the Chloride, and this we may do with impunity, since it is known that Pyroxyline, the basis of Collodion, has comparatively little effect upon the Salts of Silver, and behaves towards them almost in the manner of an inert substance, such as glass or porcelain. Having therefore taken a sample of ordinary Collodion, dissolve in each ounce seven grains of Chloride of Zinc; then coat two glass plates in the usual way, allow them to become quite dry, and immerse in a Nitrate bath. Rear one of the plates on end to drain, but wash the other with water, and pour over it a little diluted Albumen, afterwards drying a second time, and re-dipping in the bath. In the course of a few hours expose both to sun-light. It will be found that the Chloride of Silver upon Collodion alone darkens to a violet-blue tint; but that on Albumen and Collodion mixed, changes to a deep olive-brown. Now apply a drop of Nitric Acid to the two plates; the violet subchloride will be very little affected, but the brown image containing a suboxide will dissolve. Next treat the plates with Ammonia; this will dissolve the violet, and produce no effect upon the brown image. It is clear therefore, from the action of these tests, that the presence of Albumen makes an important difference in the nature and properties of the image.

But in order to investigate the subject thoroughly, the darkened plates must be examined *after*, as well as before, treatment with a fixing agent, since a photographic picture cannot be said to be completed until it has passed through the bath of Hyposulphite of Soda.

We therefore prepare a fresh series of films of Chloride and Nitrate of Silver in the manner above described—viz., some on dry Collodion, and others upon Albumen, and having, by repeated treatment with fresh Nitrate of Silver, and a long exposure to the sun's rays, obtained the maximum of darkening, we immerse them in a solution of Hyposulphite of Soda, wash carefully, and dry. Comparing the two sets of images after fixing, we find those on the Collodion, grey by reflected light, and pale slaty-blue by transmitted light. The images on the Albumen, on the other hand, are of a dark olive-brown by reflection, and almost absolutely opaque when examined by transmission. The following tests are then applied:—*a. Mercury:* amalgamation with the Collodion image, but none with the Albumen. *b. Cyanide of Potassium:* no action on the grey and transparent image, but gradual solution of the brown opaque image. *c. Sulphuretted Hydrogen water:* darkens the image on Collodion, but gradually bleaches that on Albumen. *d. Permanganate of Potash*, if in dilute solution, scarcely acts on the slaty-blue image, but oxidizes the brown image.

Putting these facts together, we conclude that photographs formed on pure Chloride and Nitrate of Silver consist of a Subchloride of Silver before fixing with Hyposulphite of Soda, and of Metallic Silver after fixing. In practice, however, it is found impossible to produce a picture on pure Chloride of Silver, the image being altogether too faint, and lacking depth of colour by reflected light. When Albumen, Gelatine, or analogous substances are present, the image contains Suboxide of Silver combined with organic matter: and this combination is not entirely destroyed in the process of fixing, for although both Subchloride and Suboxide of Silver are instantly decomposed by fixing agents, yet the latter does not appear to be so when united with Albumen.

The action of tests upon the organic image will vary with the length of time the plates have been ex-

posed to light. The more intense the blackening the less evident is the action of solvents, such as the Cyanide of Potassium, etc. Hence the half tones of a Photographic picture often dissolve in fixing, whilst the full shadows remain. Unstable Salts of Gold, on the other hand, when applied to an image on paper, deposit the metal more readily on those parts which have been completely blackened, and less so upon the lighter shades. Again, if Photographic papers be prepared with two different kinds of organic matter, as, for example, with Iceland moss in one case and Albumen in another, the images obtained will not exactly correspond in properties. And if, in a third experiment, the paper be rendered sensitive upon a solution of Ammonio-nitrate of Silver in place of Nitrate of Silver, the reaction with tests will again be different. Therefore, although the Photograph contains both organic matter and Silver, no certain formula can be given for its composition.

CHAPTER IV.

ON THE DEVELOPMENT OF AN INVISIBLE IMAGE BY MEANS OF A REDUCING AGENT.

It has been shown in the previous Chapter that the majority of the Salts of Silver, either alone or in contact with organic matter, are darkened in colour on exposure to light, and, by the loss of Oxygen, Chlorine, etc., become reduced to the condition of *Sub*salts.

Many of the same compounds are also susceptible of a change under the influence of light, which is even more remarkable. This change takes place after a comparatively short exposure, and does not affect the appearance of the sensitive layer. The impression, however, although invisible at first, is brought out by treating the plate with certain chemical agents, which are without effect on the original unchanged salt.

Experiments illustrating the Formation of an Invisible Image.—Take a sheet of sensitive paper, prepared with Iodide of Silver by the method given in another part of this work, and having divided it into two parts, expose one of them to the luminous rays for a few seconds. No visible decomposition takes place, but on removing the pieces to a room dimly illuminated, and brushing with a solution of *Gallic Acid*, a manifest difference will be observed; the one being unaffected, whilst the other darkens gradually until it becomes black.

Experiment II.—A prepared sheet is shielded in certain parts by an opaque substance, and then after the requisite exposure, which is easily ascertained by a few trials, treated with the Gallic Acid as before; in this case the protected part remains white, whilst the

other darkens to a greater or less extent. In the same way, copies of leaves, engravings, etc., may be made, very correct in the shading, and much resembling those produced by the prolonged action of light alone upon the Chloride of Silver.

A great economy of time is effected by employing a substance like Gallic Acid to *develop* or bring out to view an invisible image, in preference to forming the picture by the direct action of light, unassisted by a developer. This is well shown in the results of some experiments conducted by M. Claudet in the Daguerreotype process: he found that with a sensitive layer of Bromo-Iodide of Silver, an intensity of light three thousand times greater was required if the use of a developer was omitted, and the exposure continued until the picture became visible upon the plate.

To increase the sensitiveness of Photographic preparations is a point of great consequence; and indeed, when the Camera is used, from the low intensity of the luminous image formed in that instrument, no other plan than the one above described would be practicable. Hence the advancement, and indeed the very origin, of the Photographic art, may be dated from the first discovery of a process for bringing out to view an invisible image by means of a reducing agent.

The present Chapter is divided into two Sections:—first, the properties of the substances usually employed in reducing the Salts of Silver, with their mode of action; and second, the formation and development of the invisible image.

SECTION I.

The various Substances employed as Reducing Agents.

The most important of the developers are as follows:—Gallic Acid, Pyrogallic Acid, and the Protosalts of Iron.

GALLIC AND PYROGALLIC ACIDS.

a. *Gallic Acid.*—Gallic Acid is obtained from *Gall Nuts*, which are peculiar excrescences formed upon the branches and shoots of the *Quercus infectoria* by the puncture of a species of insect. The best kind is imported from Turkey, and sold in commerce as Aleppo Galls. Gall Nuts do not contain Gallic Acid ready formed, but an analogous chemical principle termed *Tannic Acid*, well known for its astringent properties, and employment in the process of tanning raw hides.

Gallic Acid is produced by the *decomposition and oxidation* of Tannic Acid, when powdered galls are exposed for a long time in a moist state to the action of the air. By boiling the mass with water and filtering whilst hot, the acid is extracted, and, being sparingly soluble in cold water, crystallizes on cooling.

Gallic Acid occurs in the form of long silky needles, soluble in 100 parts of cold and 3 of boiling water; they are also readily soluble in Alcohol, but sparingly in Ether. The aqueous solution becomes mouldy on keeping, to obviate which the addition of a lump of Camphor or a drop or two of Oil of Cloves is recommended.

Gallic Acid is a feeble acid, scarcely reddening litmus; it forms salts with metallic Oxides, but those of Silver and Gold are reduced by it to the metallic state.

b. *Pyrogallic Acid* (*or Pyrogallol*).—The term *pyro-* prefixed to Gallic Acid implies that the new substance is obtained by the *action of heat* upon that body. At a temperature of about 410° Fahr., Gallic Acid is decomposed, and gives off a white vapour, which condenses in lamellar crystals; this is Pyrogallic Acid.

Pyrogallic Acid is very soluble in cold water, and in Alcohol and Ether; the solution decomposes and becomes brown by exposure to the air. By adding Sulphite of Soda to an aqueous solution it remains colourless for a long time. Tannin has a similar effect,

but in a less marked degree. It gives an indigo-blue colour with Protosulphate of Iron, which changes to dark green if any Persulphate be present.

Although termed an *acid*, this substance is strictly *neutral;* it does not redden litmus-paper, and forms no salts. It has an affinity for Oxygen, which is greatly augmented by the presence of an alkali; a mixture of this kind made by adding Liquor Potassæ to Pyrogallic Acid, is often employed for absorbing the Oxygen contained in atmospheric air.

Commercial Pyrogallic Acid is often contaminated with empyreumatic oil, and also with a black insoluble substance known as *Metagallic Acid*, formed when the heat is raised above the proper temperature in the process of manufacture.

THE SALTS OF IRON.

There are two Oxides of Iron which form Salts, viz. —the Protoxide of Iron, containing an atom of Oxygen to one of metal; and the Peroxide, with an atom and a half of Oxygen to one of metal. As *half atoms*, however, are not allowed in chemical language, it is usual to say that the Peroxide of Iron contains three atoms of Oxygen to two of metallic Iron.

Expressed in symbols, the composition is as follows:

Protoxide of Iron (Ferrous Oxide), Fe,O.
Peroxide of Iron (Ferric Oxide), Fe_2O_3.

The Proto- and Per-salts of Iron do not resemble each other in their physical and chemical properties. The former are usually of an apple-green colour, and their aqueous solutions are almost colourless, if not highly concentrated. The latter, on the other hand, are dark, and give a yellow or even blood-red solution.

The following experiment will serve to illustrate the properties of both classes of salts:—Take a crystal of Protosulphate of Iron, and, having reduced it to powder, pour a little Nitric Acid upon it in a test-tube. On the application of heat, abundance of fumes

will be given off, and a red solution obtained. The Nitric Acid in this reaction imparts Oxygen, and converts the *Proto*sulphate entirely into a *Persalt* of Iron. It is this feature—viz., the tendency to absorb Oxygen, and to pass into the state of Persalts, which makes the Protosalts of Iron useful in Photography.

There are two Protosalts of Iron commonly employed by Photographers: the Protosulphate and the Protonitrate of Iron, the former being for Wet Collodion Negatives, and the latter for Positives.

a. *Protosulphate of Iron.*—This salt, often termed *Copperas* or *Green Vitriol*, is an abundant substance, and is used for a variety of purposes in the arts. Commercial Sulphate of Iron, however, being prepared on a large scale, requires recrystallization to render it sufficiently pure for Photographic purposes.

Pure Sulphate of Iron occurs in the form of large transparent, prismatic crystals, of a delicate green colour: by exposure to the air they gradually absorb Oxygen and become rusty on the surface. Solution of Sulphate of Iron, colourless at first, afterwards changes to a red tint, and deposits a brown powder; this powder is a *basic* Persulphate of Iron, that is, a Persulphate containing an excess of the oxide or *base*. By the addition of Sulphuric or Acetic Acid to the solution, the formation of a deposit is prevented, the brown powder being soluble in acid liquids.

The Crystals of Sulphate of Iron include a large quantity of water of crystallization, a part of which they lose by exposure to dry air. By a higher temperature, the salt may be rendered perfectly *anhydrous*, in which state it forms a white powder.

b. *Protonitrate of Iron.*—This salt is prepared by double decomposition between Nitrate of Baryta or Lead and Protosulphate of Iron. It is an unstable substance, and crystallizes with great difficulty; its aqueous solution is pale-green at first, but it is very prone to decomposition, even more so than the corresponding Sulphate of Iron.

c. *Proto-oxalate of Iron* (*Ferrous Oxalate*).—For dry plates prepared with Silver Bromide, Ferrous Oxalate development is much employed. Allusion has been made to its preparation in the Vocabulary, and practical details as to this and to its use will be found in a subsequent page. The solution of Potassium Oxalate, in which the Ferrous Oxalate is dissolved, takes no part in the development of the image, which being formed of metallic Silver leaves Ferrous Bromide and Ferric Oxalate as the other products of the decomposition.

Presence of Free Acids, etc., in Development.—Acids exercise a retarding effect upon the reduction of Salts of Silver by the developing agents, and especially acids, like Nitric or Sulphuric Acid, which have strong affinities for bases. Solution of Pyrogallic Acid mixed with Nitrate of Silver produces a deposit immediately, and Salts of Iron will also separate Silver before long; but if a little Acetic Acid be previously added, the precipitation is more gradual, and when both solutions are strongly acidified with Nitric Acid, it is for a time suspended. On the other hand, *alkaline* liquids produce an opposite effect, and favour quick reduction.

Comparative Strength of Reducing Agents.—Sulphate of Iron acts with rapidity. Nitrate of Iron and Gallic Acid are both feeble reducing agents. Pyrogallic Acid is stronger, a smaller quantity sufficing to produce the effect. Oil of Cloves, Grape Sugar, Aldehyde, Honey, etc., are capable of reducing Salts of Silver, but they act too slowly to be employed with advantage in Photography.

Effect of Temperature.—Reduction of the Salts of Silver proceeds more rapidly in proportion as the temperature rises. In cold weather it will be found that the development is slower than usual, and that greater strength of the reducing agent and more free Nitrate of Silver is required to produce the effect. The action of Sulphate of Iron, however, is considered to be less affected by depression of temperature than that of Pyrogallic Acid.

On the other hand, if the heat of the atmosphere be excessive, the tendency to rapid reduction will be greatly increased, the solutions decomposing each other almost immediately on mixing. In this case the remedy will be to use Acetic Acid *freely*, or in place of it Citric Acid, which, as a retarding agent, is at least twenty times stronger than Acetic Acid.

Varieties of Colour in Deposited Silver.—The precipitate of metallic Silver obtained by the action of reducing agents upon the Nitrate, varies much in colour and in general appearance. If Gallic or Pyrogallic Acid be employed, it is a black powder; whilst the Salts of Iron, and especially the same with free Nitric Acid added, produce a sparkling precipitate, resembling what is termed *frosted silver*. Grape Sugar and many of the essential oils, such as Oil of Cloves, etc., separate the metal from Ammonio-Nitrate of Silver in the form of a brilliant mirror film, and are often employed in silvering glass.

In remarking upon these peculiarities in the molecular condition of precipitated Silver, it should be observed that the appearance of a metal whilst in mass is no indication of its colour when in the state of fine powder. Platinum and Iron, both bright metals, and susceptible of a high polish, are dull and intensely black when in a fine state of division; Gold is of a purple or yellowish-brown; Mercury a dirty grey.

SECTION II.

The Formation and Development of the Latent Image.

In forming an extemporaneous theory on the production of the Photographic image by development, it would therefore be natural to suppose that the process consisted in commencing a reducing action upon the sensitive surface by means of the luminous image of the Camera, and afterwards completing or carrying on the same by the application of the developing solu-

tion. We may remark however that this hypothesis is not the one most strongly supported by facts, and that it will certainly lead us astray if too far pressed. The idea of the luminous image in the Camera orginating a chemical change, and the reducing agent carrying on that change to its completion, might lead to the inference that the two agencies were exactly similar in their mode of operation, and that the one could be substituted for the other: that when, for instance, the exposure in the Camera had been very brief, the defect would be remedied by prolonging the development. Such a notion is quite erroneous. A definite time is occupied in the formation of the invisible image, which cannot be shortened or extended beyond its proper limits with impunity. So far from the action of the developing solution being facilitated when the plate has been left in the Camera for an unusually long time, it is often retarded thereby; and, on the other hand, unless the exposure be sufficient, it will be in vain to expect to produce a picture by strengthening the reducing agent or keeping it upon the plate for a longer time. Thus we see that "the invisible image" has a real existence, and that its formation by the solar ray is a phenomenon quite distinct from any after-process of development.

HYPOTHESIS ON THE NATURE OF THE INVISIBLE IMAGE.

When a sensitive film containing a Salt of Silver is exposed in the Camera, and receives a latent impression capable of subsequent development, an inquiry arises as to the exact condition of the film-particles on which the light has acted. The most careful inspection, even with the aid of a microscope, fails to detect any difference between the exposed and non-exposed portions of the plate. Chemical solvents likewise act in the same manner both before and after the insolation, thus showing that there is no actual separation of the elements of the film, analogous to the elimination of

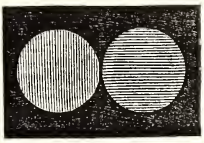
Chlorine from Chloride of Silver by the prolonged action of the sun's rays.

The formation of the invisible image is supposed to be a molecular change, unattended with any *separation* of elements such as occurs in the case of a visible image impressed by light. The following diagrams will assist mechanically in conveying an idea of what we mean by a molecular change.

Fig. 1.



Fig. 2.



Let fig. 1 represent the Iodide of Silver in its normal state, and fig. 2 the same Iodide after its impression in the Camera. The percentage composition has not been changed, for supposing one of the circles to represent Iodine and the other Silver, we have in both figures a single atom of each. The arrangement of the constituent atoms however has been modified in the second figure, where they are so placed as to touch each other only at the edges. *Let it be borne in mind that this representation is purely hypothetical.* We observe certain differences in the properties of the Iodide after its insolation, and suppose them to indicate corresponding differences in molecular arrangement; but we cannot speak with certainty, since the ultimate atoms of bodies are too minute to come within the range of our observation.

We now proceed to examine further the tangible differences between the impressed and the non-impressed atom of Iodide of Silver. If the two be exposed for a short time over Mercury slightly warmed, the metallic vapour will condense upon the former, but not upon the latter; and in this way the latent picture is made visible in the Daguerreotype process. So, again, if Nitrate of Silver previously mixed with a

reducing agent be applied to the same two atoms, it will be seen that the impressed or modified Iodide hastens the decomposition of the mixture, whereas the Iodide prepared in total darkness exercises no such effect. We have indeed learnt from the observations in the last Section that reducing agents themselves decompose Nitrate of Silver, and throw down the metal in a pure form. This reduction however is usually slow and gradual, and when a little free acid, such as Nitric or Acetic Acid, is added, the mixture remains perfectly clear for a period of five minutes or longer. Prepare therefore such a mixture with the proportions correctly adjusted, and drop into it two particles, one of the ordinary and the other of the impressed Iodide of Silver; when it will be found that the first remains yellow, but that the second immediately becomes black and is incrusted with Metallic Silver.

There are other instances of the surfaces of bodies undergoing a molecular change, not to be detected by the eye, but yet sufficient to affect the affinities of compounds brought into contact with such surfaces.

An instructive illustration of this may be conducted as follows:—Take a clean glass vessel, and having poured into it a strong aqueous solution of Chloride of Potassium, add a little Tartaric Acid, and stir briskly with a glass rod. In a few moments the parts of the glass touched by the rod will be marked by a line of minute crystals. In this case there is a disposition in the liquid to crystallize: but the *rubbed state of the glass*, where the rod has touched it, facilitates the change, and determines the point at which the crystallization shall commence. The deposit is adherent, and is not removed by emptying the capsule of its contents and washing it out with alcohol; warm water, however, dissolves the crystals of Bitartrate, and the surface of the glass is then found intact; the rubbed condition, as we have termed it, being temporary and quite invisible.

One additional illustration of molecular in contra-

distinction to chemical change will suffice. When an engraving which has been framed and suspended for a length of time is taken down to be cleaned, it will sometimes happen that the glass, however carefully polished by rubbing, will exhibit the outlines of the picture when breathed on. The breath settles in certain parts and not in others, in consequence of variations in the surface condition. When the glass is put aside, the invisible image gradually vanishes, and the molecules return to their original state.

Granting, therefore, that a ray of white light in acting on Iodide of Silver, so modifies it that it acquires the property of accelerating chemical change in the mixture known to Photographers as the developing agent, we observe, in the next place, that it is not necessary to suppose that the invisible modification is permanent, or that the particles of the Iodide, once

Fig. 3.

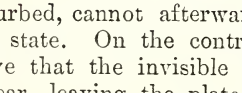
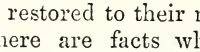


Fig. 4.



disturbed, cannot afterwards be restored to their normal state. On the contrary, there are facts which prove that the invisible image may completely disappear, leaving the plate in a condition to receive a second impression in the Camera.

Mechanical diagrams may here be again employed; and their use will be free from objection, if it be understood that they are meant only to assist in fixing facts upon the mind of the reader, and like a system of artificial memory, may be laid aside when this important object has been accomplished.

In figure 3 we see two ovals, slightly different in size, and turning on a common centre; in (*a*) their long diameters correspond, but in (*b*) they cross each other, whilst in (*c*) they are made to coincide once more by a further action of the same force. In fig. 4 we

have the more familiar illustration of waves; first an elevation, then a corresponding depression. Now in the photographic process we find that the invisible effect of the light rises gradually to a certain pitch of intensity, but beyond that it appears to descend as it were on the other side: hence the particle of Iodide of Silver first acquires the property of blackening the developer, but loses it again if left too long in the Camera.

THE DEVELOPMENT OF THE INVISIBLE IMAGE.

The amateur commencing the study of Photography will probably form an incorrect idea of the real nature of a developing agent. Being in the habit of applying to the surface of the wet Collodion a solution of Pyrogallic Acid or of Sulphate of Iron, he terms these compounds "the developers," and forgets that a floating layer of solution of Nitrate of Silver is also present, derived from the bath. To impress upon the mind the fact that the developer is not the simple reducing agent, but the same *mixed with Nitrate of Silver*, let the following experiment be made. Coat a plate with Iodized Collodion, pass it through the Nitrate Bath, and wash it carefully back and front with distilled water. Now expose for an instant to diffused daylight, and apply the Pyrogallic Acid; the plate will remain perfectly clear and transparent. The invisible impression however is truly present, and the insolated Iodide is ready to play its part, but no blackening takes place, because the reducing agent has nothing to act upon. Let the Pyrogallic Acid, therefore, be poured back into a measure containing a few drops of solution of Nitrate of Silver and applied a second time to the plate, when the film will begin to darken and continue to do so until it is quite opaque.

The Second Stage of the Development.—This consists in strengthening the image first formed, by an additional deposit of Silver. Take a sensitive Collodion

plate, and having impressed an invisible image upon it by a proper exposure in the Camera, remove it to the dark room, and pour over it solution of Pyrogallic Acid. When the picture has fully appeared, stop the action by washing the plate with water. An examination of the image at this stage will show that it is perfect in the details, but pale and translucent. Now take the plate and treat it with Pyrogallic Acid to which fresh Nitrate of Silver has been added; immediately the picture will become much blacker, and will continue to darken, even to complete opacity, if the supply of Nitrate be kept up. The same result may be obtained after the Iodide of Silver has been removed from the plate by Hyposulphite of Soda or Cyanide of Potassium; and in such a case it is evident that the additional deposit upon the image must be produced from the Nitrate of Silver and not from the Iodide of Silver. Observe also, that this additional deposit *forms only upon the image*, exhibiting no affinity for the unaltered Iodide upon the part of the plate corresponding to the shadows of the picture, but attaching itself in preference to those parts already blackened by the developer.

The second stage of the development, in which a feeble image is strengthened and rendered more opaque, is a process bearing a close resemblance to the growth of a crystal in a saturated liquid, by aggregation of fresh particles; and after the picture has reached its full density, a series of elevations may often be seen upon the plate, corresponding to the lines of the image.

OBJECTIONS TO THE FOREGOING VIEWS CONSIDERED.

The theory of the formation and development of the latent image given in the preceding pages was not originated by the author of this work, nor can he at present specify any one individual to whom it may be ascribed. Objections have been urged against it, and other hypotheses adopted in preference, not only in this country but also in France. It has been said, for instance, that the process of photographic printing upon Chloride of

Silver involves a partial reduction of the Chloride by the action of light, and hence it is reasonable to suppose that the Iodide of Silver suffers reduction in the developing process. We must bear in mind, however, that there is a great difference in the intensity of the light to which the sensitive surface is subjected in the two cases mentioned, and not only so, but that the Iodide of Silver is more difficult to reduce than the Chloride. In fact, as we have already shown, the solar ray has no effect in discolouring pure Iodide of Silver, although it quickly blackens pure Chloride of Silver. If the invisible image were simply a disturbance of ultimate particles, rendering their after-separation by the reducing agent more easy, we should expect to find Chloride of Silver receiving the image of the Camera with greater rapidity than Iodide of Silver. The contrary, however, is the case, and we are probably within the mark in stating the sensitiveness of Iodide of Silver to be ten times greater than that of Bromide and sixty times greater than that of Chloride of Silver.

Another argument militating strongly against the view often expressed that the latent image consists of Iodide of Silver reduced in inappreciable quantities, or of Iodide of Silver with an increased tendency to reduction, is the fact before mentioned, that the rapidity of the development is not in proportion to the length of the exposure in the Camera. On the over-exposed sky of a landscape the Iodide will sometimes remain yellow and unchanged throughout the whole process, whilst the less exposed parts of the plate darken under the influence of the developer.

The opponents of the views which we have given of the purely molecular character of the disturbance in the Camera, base their objections chiefly on phenomena observed in the practice of the dry Collodion processes. It is not unusual in such methods to obtain visible indications of the picture upon the surface of the film before the developer is applied; and even where no such indications present themselves, there yet often exists a

remarkable difference between the exposed and the non-exposed parts to which as yet we have not directed the reader's attention. Mr. Young, of Manchester, was the first to notice the phenomenon, and to show that if an exposed plate be immersed in solution of Hyposulphite of Soda until the yellow Iodide of Silver is dissolved, a picture will still appear on applying the usual developing mixture. The effect cannot be obtained on a wet Collodion plate and only imperfectly on a plate preserved by honey, the best substance to exhibit it being Albumen. Experiments have been made with a view of accounting for a phenomenon so remarkable as the development of an invisible image upon a plate previously cleared of its Iodide of Silver, and the explanation suggested is as follows:—Pure Iodide of Silver is molecularly modified by the Camera image, but its properties as regards the action of Hyposulphite of Soda are unaffected thereby: upon a plate so constituted no image could be developed after fixing. The sensitive surface of the Collodion film is never, however, an absolutely pure Iodide of Silver, and sometimes very far from being so. It contains traces of an organic compound of Silver in the wet Collodion process, and more appreciable quantities of the same in the dry processes. Now, with a compound film of this kind, it may be supposed that whilst the Iodide of Silver undergoes its peculiar change in the Camera, the organic combination of Silver likewise changes, but in a different manner. Without altering in appearance, it gradually loses its solubility in fixing agents, so that when the Hyposulphite of Soda is applied its removal is not effected. We do not, however, perceive any picture upon the film, because the organic combinations of Silver are transparent in thin layers, even when they contain Iodide of Silver. An Albumino-Iodide of Silver, for instance, may be prepared in clear and colourless lumps like the finest jelly, and it is not difficult to conceive that such a substance may remain in an invisible condition upon Mr. Young's plates even after fixing.

If the above hypothesis be correct, there exist two varieties of the invisible image: first, that upon simple Iodide of Silver, which enables it to condense Mercury or to determine chemical change in the unstable developer; secondly, the image upon Iodide of Silver placed in contact with an organic compound of Silver. In the latter case the movement of the particles of the Iodide is supposed to be propagated to the other body, and changes are thus originated, visible or latent, according to the duration of the exposure, and the properties of the superadded substance. An organic Salt of Silver contains in itself the elements of its own reduction, and hence we are not surprised to find a catalytic action exerted upon it by the actinically excited Iodide of Silver.

CAUSES WHICH AFFECT THE SENSITIVENESS OF IODIDE OF SILVER.

By the term sensitiveness we understand a facility of receiving an impression from a very feeble ray of light, or of receiving it quickly from a bright ray. This impression, however, need not be followed by a vigorous or intense development, in order to constitute sensitiveness. On the contrary, it often happens that the most sensitive film yields a feeble picture, and when the Iodide is so prepared as to produce an opaque picture, then it is less sensitive, and requires to be exposed in the Camera for a longer time.

It has already been stated that although Iodide of Silver is less affected by direct sunlight than Bromide or Chloride of Silver, yet that it is more sensitive to the reception of the invisible image than either of those compounds. Placing Iodide of Silver, therefore, at the head of the list, we remark that, in the state in which it is used upon Collodion, it possesses the highest degree of sensitiveness when there is an excess of Nitrate of Silver; and if the experiment be made of washing the plate carefully with distilled water so as

to remove the free Nitrate, a longer exposure in the Camera will be required. The sensitiveness does not, however, increase uniformly with the amount of free Nitrate, and it has been found in the Collodion process that no advantage can be gained by using a solution of Nitrate of Silver stronger than that usually recommended for the Bath.

Strong acids, like Nitric Acid, greatly diminish the sensitiveness of Iodide of Silver. Even a weak vegetable acid, such as the Acetic, has a similar though less decided effect, and if the Collodion film be rendered very acid with Acetic Acid before its exposure in the Camera, it will be found impossible to take a picture rapidly, even after strengthening the developer to the utmost limit.

It has long been remarked that the use of bodies like Albumen, Gelatine, Caseine, etc., which combine with Oxides of Silver, retards the action of light upon Iodide of Silver; and one principal reason why the Collodion film is so sensitive is believed to be that Pyroxyline, the basis of Collodion, is a substance peculiarly indifferent to the Salts of Silver, and exhibits very little tendency to combine with them. The Photographer often employs Albumen, but he does so with a view of increasing the opacity of the image, and not for the purpose of adding to the sensitiveness. Whilst discussing Mr. Young's experiments, we have distinguished between simple Iodide of Silver and Iodide with addition of organic compounds. The latter combination gives the more vigorous picture, but the former is superior in sensitiveness.

The great sensitiveness of Iodide of Silver in Collodion may also be due in a measure to mechanical causes. The loose state of coagulation in a Collodion film and the exquisitely fine state of division in which the particles are deposited must be favourable to molecular and chemical change. It will be seen as we proceed that success in this process depends very much upon correctly balancing the different solutions, in order

that the Iodide of Silver may be thrown down in a state favourable to penetration by the developer.

Before passing to the next division of our subject, it may further be remarked, that in any Photographic process in which an invisible image is produced, the time occupied in forming that image will vary more or less with the nature of the agent by which it is to be developed. Bodies like the Protosulphate of Iron, possessing a strong affinity for Oxygen, will throw down Metallic Silver upon a surface of Iodide of Silver which has not undergone a sufficiently decided modification in the Camera to be affected by a weaker developer like Gallic Acid. It is probable that the future of instantaneous Photography lies in the discovery of a developer even more unstable than a mixture of Sulphate of Iron and Nitrate of Silver; for the greater the instability, the less the need of a previously disturbing force to originate motion in the particles.

The controlling influence of the developer upon the sensitiveness of Iodide of Silver, must be borne in mind in instituting comparisons between the Daguerreotype and the Collodion process. The employment of *Bromine* in conjunction with Iodine increases the sensitiveness of the Daguerreotype, but we have no reason to suppose that such would be the case if the image were developed in a different manner. The vapour of Mercury condenses more readily upon the insolated *Bromo*-iodide than upon the simple Iodide of Silver, but another vapour might condense less readily, and experiment is the only safe guide.

Whilst upon this subject, we also remark that the Iodide of Silver formed on a Daguerreotype plate ought not to be compared photographically with Iodide of Silver thrown down from aqueous solutions. In the case of the metal plate there is a substratum of Metallic Silver, and it is not certain that the composition of this Iodide corresponds to that precipitated in the moist way. The action of light upon it certainly

differs, for whereas the humid Iodide remains unaffected in the sun's rays, the Iodide of the Daguerreotypist gradually becomes insoluble in solution of Hypo-sulphite of Soda.

RESEARCHES OF M. MOSER AND OTHERS ON INVISIBLE IMAGES.

The papers of M. Ludwig Moser "On the Formation and Development of Invisible Images," published in 1842, explain so clearly many remarkable phenomena of occasional occurrence in the Photographic processes, that no apology need be offered for referring to them.

His first proposition may be stated thus:—"If a polished surface has been touched in particular parts by anybody, it acquires the property of precipitating certain vapours on these spots differently to what it does on the other untouched parts." To illustrate this, take a thin plate of metal, having characters *excised*: warm it gently, and lay it upon the surface of a clean mirror glass for a few minutes: then remove, allow to cool, and *breathe* upon the glass, when the outlines of the device will be distinctly seen. A plate of polished Silver may be substituted for the glass, and in place of developing the image by the breath, it may be brought out by Mercurial vapour.

The second proposition of M. Moser was as follows:—"*Light* acts on bodies, and its influence may be tested by vapours that adhere to the substance." A plate of mirror glass is exposed in the Camera to a bright and intense light; it is then removed and breathed upon, when an image before invisible will be developed, the breath settling most strongly upon the parts where the light has acted. A plate of polished Silver may be used as before instead of glass, the vapour of Mercury or of water being employed to develop the image. A Silver plate exposed to the vapour of Iodine until Iodide of Silver has formed upon its surface, is still more sensitive to the influence of light, and receives a

very perfect impression under the subsequent action of the Mercury.

The above and other experiments of M. Moser have a practical significance, for it has since been found that the same condition of surface which causes a vapour to settle in a peculiar manner may also affect the behaviour of the Iodide of Silver when treated with a mixture of Nitrate of Silver and a reducing agent. Thus, if a clean glass plate be touched in certain spots by the warm finger, the impression soon disappears, but is again seen on breathing upon the glass; and if this same plate be coated with a very delicate layer of Iodized Collodion and passed through the Nitrate bath, the solution of Pyrogallic Acid will often produce a well-defined outline of the figure even before the plate has been exposed in the Camera. This experiment is an instructive one, and shows the necessity of cleaning the plates used in Photography with care. If there be any irregularity in the manner in which the breath settles upon the glass when it is breathed on, a condition of surface exists at that point which will probably so modify the layer of Iodide of Silver, that the action of the developing fluid will be in some way interferred with.

Glass plates with Collodion pictures on them should be cleaned very carefully before being again used, or the old impression will re-appear during development. Plates packed in sheets of newspaper often show the letters in the same way when the Pyrogallic Acid is applied: traces of organic matter in all probability are present on the surface of the glass, and it is only by long soaking in chemical solutions that these invisible images can be destroyed. It may in every case be assumed that the existence of the invisible image can be detected by breathing, and that a glass which does not affect the breath is photographically clean.

M. Moser in the same series of papers calls attention to the peculiar phenomena resulting from over-action of light. "If light," he says, "acts on Iodide of Silver,

it imparts to it the power of condensing mercurial vapours, but if it acts beyond a certain time, it then diminishes this power, and at length takes it away altogether." This observation, like the last, is a practical one, for in all photographic processes we have to contend against the phenomenon known as solarization. Over-exposure in the Camera will invariably weaken the action of the developer more or less, but nevertheless the tendency to solarize may be overcome in a measure by associating other substances with the Iodide of Silver, so as to impart greater stability to the invisible image. Bromide of Silver appears to exercise such an effect, as also does an acid condition of the film. The presence of organic Salts of Silver in the film likewise influences the amount of solarization.

Observations by Norris and others.—When a sensitive Collodion plate is washed in water before its exposure in the Camera, a mixture of Pyrogallic Acid and Nitrate of Silver is required to develop it. The mixture is usually made before the developer is applied to the film, and this is of more importance than would appear. If the Pyrogallic Acid solution be used alone without any Nitrate of Silver, it will frequently *obliterate* the latent impression, so that a second picture may be taken upon the same plate. Such, however, is not invariably the case; if a mere trace of Nitrate of Silver remain in the pores of the Collodion, there will be development instead of obliteration. A washed Collodion film may have its free Nitrate of Silver restored to it by dipping in the Bath after exposure, but it will, as a rule, develop with unusual energy after such treatment, and the picture will be taken by a shorter exposure than if the plate were simply flooded with a mixture of Pyrogallic Acid and Nitrate of Silver.

Dilute acids gradually obliterate the latent image on washed Collodio-iodide of Silver. When an exposed plate is left for a time over the vapour of Acetic Acid, the impression gradually disappears and the film returns to a sensitive condition. On repeating this

experiment, the author finds that the second latent image requires a longer exposure in the Camera, and develops in a somewhat different manner from the first.

Dry Iodide of Silver on Collodion, gradually loses its power of receiving the latent image, when placed in contact with certain other bodies. Thus the extreme edges of dry plates, where they touch the grooves of the carrying-box, often remain transparent on developing, and exhibit no indications of an impression. Traces of organic matter have a similar effect on the Iodide in the wet process, as may be proved by allowing a drop of saliva to fall on a glass plate, and then carefully removing it with a silk handkerchief. On Collodionizing the glass and passing it through the Nitrate Bath, there will be a transparent mark of defective development on that particular part, showing that the Iodide had not undergone the usual change in the Camera.

Grove's Electrical Images.—Mr. Grove has succeeded in producing latent images by electricity. In the experiments described, a plate of glass was electrized in certain parts, and then breathed on or exposed to the fumes of Hydrofluoric Acid; in either case the vapour settled exclusively upon the *non*-electrical part of the glass. When the glass was first electrized, and afterwards coated with Iodide of Silver and exposed to light, Pyrogallic Acid produced no reduction.

Experiments of Busk and others.—Mr. Busk has stated that ordinary writing-paper sensitized with Nitrate of Silver undergoes an invisible change when placed in contact with certain surfaces; and that in consequence of this change the paper loses its property of being darkened by exposure to light. To exhibit the phenomenon in perfection he recommends that the Nitrate Bath should be rather strongly acidified with Tartaric or Acetic Acid. A few hours' contact with an engraving will then produce the effect, and those portions of the sensitive paper which have been touched by the blacks of the engraving will remain white in

the solar ray, whilst the other untouched parts will darken in the usual manner.

Mr. Malone observes with reference to the above, that much depends upon the composition of the colouring-ink of the engraving, and that one kind of ink will suspend the reducing process in a sensitive paper, whilst another will fail in doing so. His mode of procedure is as follows:—The paper is rendered sensitive upon a neutral Nitrate Bath, and is then placed between the leaves of a book. Spontaneous darkening gradually ensues, but the parts opposite to the black letters remain white, in consequence of some unexplained influence exerted by the ink.

Invisible Images produced by the Agency of Ozone.—M. Thenard has shown that ordinary paper exposed to a current of ozonized Oxygen, experiences a change not visible to the eye, but becoming so when the paper is laid in contact with a sensitive sheet containing Chloride and Nitrate of Silver; blackening of the Nitrate takes place opposite to the ozonized surface. When the ozonized paper is enclosed in a damp tube, a peculiar odour is gradually developed, due in all probability to an oxidation of the organic matter into a body resembling Aldehyde or Formic Acid in its property of reducing Nitrate of Silver to the metallic state. These experiments of M. Thenard were undertaken in consequence of the publication of a series of observations by M. Niépce de St. Victor, attributing similar effects to the agency of latent light. The ingenuity of M. Niépce is praiseworthy, but the opinion entertained at the present time appears to be that the phenomena he has described are susceptible of a simpler explanation than that involved in the supposition of stored-up light.

CHEMICAL NATURE OF DEVELOPED IMAGES.

Photographic pictures obtained by developing an invisible image with a reducing agent, contain usually

a far larger quantity of metallic Silver than those produced by the long-continued action of light alone. Hence they are less easily injured by destructive agents, such as Cyanide of Potassium, Oxidizers, etc. The plan which has been adopted to ascertain the actual quantity of Silver present in an image, is first to convert the deposit into Chloride of Silver, and afterwards into Sulphide of Silver, by immersion in a solution of a soluble Sulphide. The more opaque the image appears after this treatment, the greater the quantity of real Silver.

Developed images vary, however, materially in their nature and properties, according to the circumstances under which they were produced. Photographic prints, for instance, taken on Chloride of Silver, by development after a moderate amount of exposure, resemble very closely images obtained by the direct action of light alone, whilst images like Collodion Positives are essentially different, and do not react in the same manner with tests. The former, indeed, may be compared to images formed by direct sun-light upon Chloride of Silver combined with organic matter; but the latter to images upon *pure* Chloride of Silver, which, as before shown, consist, after fixing, of metallic Silver only. The following conditions may be mentioned as affecting the character of the developed image:

a. *The Surface used to Sustain the Sensitive Layer.*—Albumen and Gelatine are favourable to the production of a brown and opaque image, which will bear magnifying without showing separate particles. Cyanide of Potassium and Oxidizing agents dissolve this image, and it will not amalgamate with Mercury. It is probably not metallic, but partly organic in its nature. Collodion, on the contrary, often gives a grey and slaty image, the ultimate particles of which are seen on magnifying. It amalgamates with hot Mercury, but is little affected by fixing agents and oxidizers. This image is nearly or quite metallic.

Certain organic matters may be dissolved in the Collodion, and the result will be to produce an image intermediate in properties between the two last described. Glycyrrhizine and Grape Sugar may be mentioned in illustration.

b. *The Nature of the Sensitive Salt.*—Bromide of Silver added to the Iodide in an Albumen or a Gelatine process, produces an image with increased opacity, and one which from the action of tests we conclude to be more organic in its nature. Bromide of Silver in Collodion, however, diminishes the intensity, and renders the image grey and metallic. In Collodion containing certain kinds of organic matter purposely added, Bromide behaves in the same manner as in Albumen, *increasing* the opacity of the developed image.

In the case of Chloride of Silver employed to receive a latent image, and supported by a surface of Gelatine or Albumen, the impression is usually slightly visible before development; and when such is the case, the resulting picture will be organic in its nature, and behave with tests more in the manner of an ordinary Photographic paper darkened by light.

c. *The Developing Agent employed.*—This subject has already been noticed. Organic developers, Gallic and Pyrogallic Acids, tend to produce images of the opaque kind; but the inorganic protosalts of Iron, grey and metallic images. *Acetate* of Iron resembles Pyrogallic Acid in its action more than it resembles the Sulphate of Iron.

The addition of a strong acid like Nitric Acid to the developer, produces a deposit, the particles of which are large and crystalline, with small opacity by transmitted light; but an alkaline condition of the solutions is favourable to a brown deposit, with the particles in a state of fine division.

d. *The Stage of the Development.*—The red image first formed on the application of the developer to a gelatinized or albumenized surface of Iodide of Silver is less metallic, and more easily injured by destructive tests,

than the black image, which is the result of prolonging the action. Developed Photographic prints, when of a bright red colour after fixing, correspond in properties to those obtained by the direct action of light on paper prepared with Chloride of Silver, and less closely to Collodion, or even to fully developed Talbotype Negatives.

e. *The Intensity of the Light by which the Invisible Image was formed.*—A very strong light acting for a short time, is followed by the development of the red image, the particles of which are finely divided, and easily acted on by solvents and oxidizing agents. A dull light, on the other hand, acting for a longer time, is succeeded by an image of the metallic variety, which amalgamates with Mercury. The two varieties of deposit may often be seen on the same picture, the former in the high lights, as the sky, the latter in the deep shadows where the chemical rays are feeble.

ILLUSTRATIONS OF ABNORMAL DEVELOPMENT.

The characteristics of the proper development of a latent image are—that the action of the reducing agent should cause a blackening in the parts touched by light, but produce no effect upon those which have remained in shadow. In operating both on Collodion and paper, however, we find a liability to failure in this respect; the film beginning, after the application of the developer, to change in colour to a greater or less extent over the whole surface.

Let us see how the above defect, known to the Photographer as "fogging," may be originated. Supposing the invisible image to be duly formed, it is yet necessary for its correct development that a proper balance should be maintained between the constituents of the developer. The reducing agent must not be too powerful, nor the quantity of Nitrate of Silver too large, otherwise, although the deposited Silver will fall principally upon the image, a portion of it will be

thrown down upon the shadows. It will also be found that the quantity of Nitrate of Silver being correctly balanced, fogging will certainly ensue if a little of this Nitrate be changed into *Oxide* of Silver by the addition of an alkali, since the tendency to reduction is then so strong that it cannot be controlled. Even when the Nitrate is accurately neutral, care and avoidance of all disturbing causes will be required to prevent a deposition of Silver upon the shadows of the image ; especially when Nitrite of Silver or Acetate of Silver are present, both of which salts are more easily reduced than the Nitrate of Silver.

The use of *Acid* is the principal resource in obviating cloudiness of the image. Acids lessen the facility of reduction of the salts of Silver by developing agents, and hence when they are present the metal is deposited more slowly, and only on the parts where the action of the light has so modified the particles of Iodide as to favour the decomposition : whereas, if acids be absent, or present in insufficient quantity, the equilibrium of the mixture of Nitrate of Silver and reducing agent which constitutes the developer is so unstable, that any rough point or sharp edge becomes a centre from which the chemical action, once started, radiates to all parts of the plate.

Observe, however, that although we employ free acids in the developer to regulate the process and prevent the chemical actions from running riot, yet if we carry the proportion of the acid too far, or employ too strong an acid, we may originate the very defect we wish to avoid. Excess of Nitric Acid is a cause of fogging, if not as potent as excess of alkali, yet very decided. In this case the opposition to reduction is so strong, that for a long time after applying the developer to the plate no Silver is deposited : eventually spangles of metal are seen, which adhere like sparkling dust to the shadows.

A more or less evident amount of fogging must be anticipated when the exposure in the Camera has been

too short. The latent image being in such a case very weak and imperfectly formed, does not act properly in attracting the Metallic Silver from the developer. When Nitrate of Silver and a reducing agent are present at the same time upon a film, Metallic Silver must very shortly fall upon some portion of the plate; hence the best security against fogging is a vigorous latent image, because in that case the action is so rapid upon the exposed parts that the energy of the developer is soon spent. Those films of Iodide of Silver which are prepared with especial reference to the production of vigorous images always give clean pictures, whereas the more sensitive Iodide of Silver is very liable to fog, since the latent image, although quickly formed, is not very deep or decided.

Spots upon the plate are instances of abnormal development, which may often be explained in a similar manner. In such a case the latent image upon the Iodide of Silver is not always sufficiently vigorous to exhaust with rapidity the mixture of reducing agent and Nitrate of Silver which constitutes the developer. Each spot exhibits, it is true, a central nucleus of extraneous matter, but this does not invalidate the argument. Such microscopic nuclei are always present upon the sensitive film to a greater or less extent, but if the invisible image be well formed, they are not so liable to increase in size during development. Full occupation must, so to speak, be provided for the developer, otherwise it will search out these minute particles, and surround them with deposited Silver. Filtering of solutions and avoidance of dust are useful remedies for spots, but so likewise is attention to the state of the sensitive film as regards vigorous and intense development. If, however, the energy of development be too great, the spots may recur; just as fogging of the film is sometimes due to deficiency of acid, and sometimes to excess of acid.

CHAPTER V.

FIXING AGENTS.

A SENSITIVE layer of Chloride or Iodide of Silver on which an image may be formed, either with or without the aid of a developing agent, must pass through further treatment in order to render it indestructible by diffused light. The image itself is sufficiently permanent, and cannot be said, in correct language, to need *fixing;* but the unchanged Silver Salt which surrounds it, being still sensitive to light, tends to be decomposed in its turn, and by darkening, to obliterate the picture.

In order that any body may be employed with success as a fixing agent, it is required not only that it should dissolve unchanged Chloride or Iodide of Silver, but that it should produce no injurious effect upon the image. A solvent action upon the image is most liable to happen when the agency of light alone, without a developer, has been employed: in that case the darkened surface, not being reduced perfectly to the metallic state, remains soluble to a certain extent in the fixing liquid.

AMMONIA AND OTHER FIXING AGENTS.

Ammonia.—Ammonia dissolves Chloride of Silver readily, but not Iodide of Silver: hence its use is necessarily confined to the direct sun proofs upon paper. Even these, however, cannot advantageously be fixed in Ammonia unless a deposit of *Gold* has been previously produced upon the surface by a process of "toning," presently to be explained: an unpleasant *red tint* is always caused by Ammonia acting upon the

darkened material of a sun picture as it comes from the printing-frame.

The principal objections to the use of Ammonia as a fixing agent are its pungent odour, and also the fact that it is scarcely strong enough in its affinities to dissolve the Oxide of Silver when associated with Albumen and similar bodies.

Chloride and Iodide as Fixing Agents.—The Chlorides of Potassium, Ammonium, and Sodium possess the property of dissolving a small portion of Chloride of Silver. In the act of solution a *double salt* is formed, a compound of Chloride of Sodium with Chloride of Silver, which may be crystallized out by allowing the liquid to evaporate spontaneously. The earlier Photographers employed a saturated solution of common Salt for fixing paper prints; but the fixing action of the Alkaline Chloride is very slow and imperfect.

The Iodide of Potassium has been used as a fixing agent for Iodide of Silver. It dissolves it by forming a double salt in the manner before described.

It is important to remark in the solution of the insoluble Silver Salts by Alkaline Chlorides, Iodides, etc., that the amount dissolved is not in proportion to the *quantity* of the solvent, but to the degree of concentration of its aqueous solution. The reason is that the double salt formed is *decomposed* by a large quantity of water. Hence it is only a saturated solution of Chloride of Sodium which possesses any considerable power of fixing; and with the Iodide of Potassium the same rule holds good—the stronger the solution the more Iodide of Silver will be taken up by a given weight. The addition of water produces milkiness and a deposit of the Silver Salt previously dissolved.

HYPOSULPHITE OR THIOSULPHATE OF SODA AS A FIXING AGENT.

Thiosulphuric Acid, $H_2S_2O_3$, formerly called Hyposulphurous Acid, S_2O_2, is one of the Oxides of Sulphur.

It is, as its name implies, of an acid nature, although the acid itself is scarcely known, for it cannot be isolated.

The Hyposulphite of Soda employed by Photographers is selected as being more economical in preparation than other Hyposulphites adapted for fixing. It occurs in the form of large translucent groups of crystals, which include five atoms of water. These crystals are soluble in water almost to any extent, the solution being attended with the production of cold; they have a nauseous and bitter taste.

Hyposulphite of Soda is now made on an extensive scale, and sold at a low price. It is usually sufficiently pure in the state in which it comes from the manufacturers.

In the solution of Silver compounds by Hyposulphite of Soda a double decomposition always takes place; thus:—

Hyposulphite of Soda + Chloride of Silver
= Hyposulphite of Silver + Chloride of Sodium.

The Hyposulphite of Silver combines with an excess of Hyposulphite of Soda, and forms a soluble double salt, which may be crystallized out by evaporating the solution. This compound possesses an intensely sweet taste, and contains one atom of Hyposulphite of Silver, with *two* of Hyposulphite of Soda. In addition to this there is a second double Salt, differing from the first in being *very sparingly* soluble in water; it contains single atoms of each constituent.

The quantity of Chloride of Silver which Hyposulphite of Soda will easily dissolve may be stated roughly as about one-third of its weight. If the proportion of Chloride be increased to more than one-half of the Hyposulphite, there will usually be an abundant deposition of minute sparkling crystals, since the second or sparingly soluble double salt of Hyposulphite of Silver and Soda will then be formed.

When Hyposulphite of Soda is employed as a fixing agent it is a safe precaution to convert any Nitrate of Silver which may be present into Chloride of Silver, otherwise there will be a danger of the solution becoming discoloured from a decomposition into Sulphide of Silver. This change will be explained more particularly in the Section on the fixing of paper proofs.

Iodide of Silver is dissolved by Hyposulphite of Soda more slowly than Chloride of Silver, and the amount eventually taken up is far less—one part by weight of Iodide of Silver requiring about twenty-four parts by weight of Hyposulphite of Soda in a cold solution; but if the solution be heated, a much larger quantity of Iodide of Silver is dissolved.

CYANIDE OF POTASSIUM AS A FIXING AGENT.

The Cyanide of *Potassium* is the salt most frequently employed in fixing, but Cyanide of Sodium will answer the purpose equally well. Cyanide of Potassium, the commercial manufacture of which is described in the Vocabulary, occurs in the form of fused lumps of considerable size. In this state it is usually contaminated with a large percentage of Carbonate of Potash, amounting in some cases to more than half its weight. By boiling in proof Spirit the Cyanide may be extracted and crystallized, but this operation is scarcely required as far as its use in Photography is concerned.

Cyanide of Potassium absorbs moisture on exposure to the air. It is very soluble in water, but the solution decomposes on keeping; changing in colour and evolving the odour of *Prussic Acid*, which is a Cyanide of Hydrogen. Cyanide of Potassium is highly poisonous, and must be used with caution.

Solution of Cyanide of Potassium is a most energetic agent in dissolving the insoluble Silver Salts; far more so than the Hyposulphite of Soda. The Salts are in all cases converted into Cyanide, and exist in the solu-

tion in the form of a soluble double Salt, which, unlike the double Sulphocyanide, is not decomposed by dilution with water. Cyanide of Potassium is not adapted for fixing Positive proofs upon Chloride of Silver; and even when a developer has been used, unless the solution of the Cyanide is tolerably dilute, it is apt to attack the image, converting it superficially into Cyanide of Silver, and then dissolving it in the form of a double Cyanide of Potassium and Silver.

The solvent powers of Cyanide of Potassium on Metallic Silver are much increased by the addition of a little Iodine to its aqueous solution; a colourless liquid is formed, which has been termed "Iodo-cyanide of Potassium."

SULPHOCYANIDES AS FIXING AGENTS.

Sulphocyanides of Potassium and Ammonium have been proposed as fixing agents; they resemble the alkaline chlorides used for this purpose, inasmuch as their solvent power *depends on the degree of concentration of the solution*, but they greatly exceed the latter salts in their power of dissolving the insoluble Salts of Silver, when strong solutions are used.

Though inferior to Hyposulphites in this varying degree of solvent power, they have the advantage of imparting no Sulphur to the print, and they preserve the tones clear and free from mealiness. They are not in favour with practical photographers.

OBSERVATIONS ON THE RELATIVE AFFINITIES OF CHLORINE, IODINE, AND HYPOSULPHUROUS ACID FOR SILVER.

Hyposulphurous (Thiosulphuric) Acid is usually viewed as a body possessing extraordinary affinities for Silver, inasmuch as a solution of Hyposulphite of Soda decomposes both Iodide and Chloride of Silver. It may be shown, however, on the other hand, that a solution of a Chloride or an Iodide will

decompose Hyposulphite of Silver under some circumstances: and hence the relative affinities are less evident than may appear. The use of these fixing agents, indeed, depends upon their being present in large excess over the Salt of Silver to be dissolved, in order that a true double salt may be formed. When two different fixing agents are employed in a state of mixture, that particular one may prevail which is present in largest quantity, even although its affinities for Silver are weaker than those of the other.

Thus, although Chloride of Silver dissolves easily in solution of Hyposulphite of Soda, we find that Hyposulphite of Silver is decomposed and converted into Chloride of Silver when treated with a saturated solution of Chloride of Sodium. And the same remark applies to Iodide of Silver; it is decomposed by a large excess of Hyposulphite of Soda, but not by a small excess. The addition of Iodide of Potassium to a fixing bath of Hyposulphite nearly saturated with Silver Salt, will precipitate a portion of the Silver in the form of the yellow Iodide of Silver.

CHAPTER VI.

THE MANUFACTURE OF PHOTOGRAPHIC COLLODION.

In order to conduct the manufacture of Collodion with success, a number of minor points must be considered, which could not conveniently be included in the general description already given. These relate not only to the Pyroxyline, but also to the Solvents and the iodizing compounds: they will now be explained with as much fulness as possible.

The most important point is the composition of the Nitro-Sulphuric Acid, in which the Pyroxyline is prepared; for it will be found that the slightest variation in the quantity of water; in the relative proportions of the two constituent acids; or in the temperature at the time of putting in the Cotton, will affect the result. It will be advisable therefore to examine these matters separately, and in addition to speak of the condition of the fibre itself, which is important both chemically and mechanically.

a. *Effect of varying the proportion of Water in the Nitro-Sulphuric Acid.*—When many separate quantities of Pyroxyline are made in the same Nitro-Sulphuric Acid, the mixture becomes gradually weaker by the abstraction of the elements of water from the fibre, and each successive portion of Pyroxyline is less in the state of explosive Gun Cotton, and more in that of Xyloidine, than the one which preceded it.

There is considerable difference in the physical properties of Collodions made from strong and weak samples of Pyroxyline prepared as above described. In the first instance, when the product is only one step removed from Gun Cotton, the Collodion pours slowly upon the glass, and tends to thicken at the edges. The film is not very adherent, and will sometimes split

away on drying. In attempting to coat a large plate, a wavy appearance, often known as *woolliness* of the film, is seen at the lower corner. With Pyroxyline made in weak acids, on the other hand, the Collodion is more limpid and free from structure, the film of Iodine when formed in the Bath presenting an even appearance throughout.

When the amount of water in the Nitro-Sulphuric Acid is carried still further, one of two things happens; either the Cotton instantly dissolves in the acid, or it is more or less disintegrated without actually dissolving. The product in the latter case is not entirely soluble in Ether and Alcohol, but leaves behind a residue consisting in part of unaltered Cotton fibre.

Here it may be proper to explain the reason why a weak Nitro-Sulphuric Acid sometimes dissolves the Cotton, and sometimes merely disintegrates it. Supposing the temperature and the Cotton used to be the same, yet the solvent action of the acid will vary with the relative proportions of Sulphuric and Nitric Acid present, even although the amount of water be correctly adjusted to that of the Sulphuric Acid. Thus a warm diluted Nitric Acid used alone acts upon the the Cotton rapidly and dissolves it; but if a very small portion of diluted Sulphuric Acid be added, the tendency to dissolve the Cotton is lessened, or if the Cotton be already dissolved the diluted Sulphuric Acid throws it down again. If, however, the proportion of the diluted Sulphuric Acid be very considerably increased, until it reaches to as much as three times the bulk of the diluted Nitric Acid, then the tendency to dissolve the Cotton becomes greater than in the case of a mixture containing equal volumes of the two diluted acids.

b. *A peculiar Action of the Oil of Vitriol in the Process.*—To demonstrate this, take a sheet of ordinary bibulous paper, and having cut it into separate pieces, float them upon Sulphuric Acid diluted with half its bulk of water and cooled: allow five seconds for the first, ten for the second, twenty for the third, and so on, until the last piece is gelatinized and dissolved;

then remove the Sulphuric Acid carefully by washing, and convert them into Pyroxyline. A marked difference will be perceptible between the samples of Collodion so obtained. The first noticeable effect of the previous parchmentizing will be an increased fluidity and freedom from structural lines. The Collodion, when poured upon a glass, sets very rapidly, and with such firmness that the finger may be rubbed backwards and forwards without disturbing it. The film on lifting from the Bath soon becomes partially surface-dry, and repels developers or fixing agents; when washed with water and dried, it forms a dense and highly-varnished surface nearly impenetrable by liquids. The moist film, after development with Pyrogallic Acid and fixing, appears unusually *tough*, and will bear pumping on without injury. It is also very contractile, and tends to draw itself away from the edges of the glass. When pushed aside it can be pulled back again like the finger of a glove. The fixing agent never removes any portion of the image from this Collodion because the Iodide of Silver is *in* the film and not only upon its surface.

The above-mentioned properties, imparted by the preliminary action of Oil of Vitriol, are not seen to an equal extent in all the pieces of paper used in the experiments, but are more decidedly evident in proportion to the time during which the acid was allowed to act. If, however, the action of the acid be carried to that point at which the paper begins to soften and become semi-gelatinous, then the resulting Collodion will be entirely different, the film being rotten and powdery. This we shall presently show to be due to a disintegration by the Nitric Acid contained in the Nitro-Sulphuric Acid, which disintegration is exhibited more strongly when the fibre is previously changed, nearly into dextrine, by the prolonged action of Sulphuric Acid.

In addition to these effects produced by parchmentizing the fibre in different degrees before converting it into Pyroxyline, there are others which deserve notice. The solubility of the product in Ether and Alcohol is much increased, so that the exact amount of water in

the Nitro-Sulphuric Acid becomes a point of less importance as affecting solubility, and an acid strong enough to make ordinary paper explosive and insoluble, answers perfectly in the case of paper previously parchmentized.

To secure the parchmentizing action in the ordinary process of making Pyroxyline, the amount of diluted Sulphuric Acid present in the Nitro-Sulphuric Acid should be considerably greater than that of the Nitric Acid. The Cotton then shrinks into a small compass, and the resulting Collodion will be tough and strong. The action of the Oil of Vitriol in the process evidently precedes that of the Nitric Acid, since we find that cotton fibre which has once been converted into Pyroxyline is no longer affected by diluted Sulphuric Acid, even when immersed for several hours.

A peculiar Action of the Nitric Acid in the process of making Pyroxyline.—The proper action of Nitric Acid in this process is, as before shown, to communicate Peroxide of Nitrogen to the fibre, and so to convert the Cellulose into Pyroxyline; the stronger the Nitric Acid, the greater the amount of peroxide imparted. We notice, however, another action of Nitric Acid upon Pyroxyline, by which the properties of the latter are much altered. This second or modifying action, if we may so term it, is exerted not so much by a concentrated, as by a diluted Nitric Acid, and more by a hot Nitric Acid than by the same acid employed cold. To exhibit this secondary action of Nitric Acid, take ordinary Pyroxyline made by the formulæ given in another part of this Work, and dip it for an instant in Nitric Acid of sp. gr. 1·45, mixed with a third of its bulk of Sulphuric Acid (to prevent it from dissolving the cotton) and heated to about 140° or 150° Fahrenheit.* The following are the main characteristics of

* In addition to this modified Pyroxyline produced by hot Nitric Acid mixed with a little Sulphuric Acid, a remarkable change of properties may be produced by the pure Nitric Acid of 1·45 employed cold, and without any admixture of Sulphuric Acid. The Pyroxyline gradually becomes opaque, and loses its solubility in Ether and Alcohol; eventually it dissolves in the cold Nitric Acid without any evolution of gas, and if water be then added, opaque white flakes are thrown down, which, when treated with Ether and Alcohol, simply swell up without passing into solution.

Collodion prepared from Pyroxyline so treated:—It does not set rapidly upon the glass like the parchmentized Collodion last described, but remains liquid for a minute, or even longer, after which it rubs under the finger in a soapy manner, instead of bearing friction without injury. After passing through the Bath the film is creamy, retains its surface-moisture for an unusually long time, and on washing with water and drying presents a porous surface, quite lustreless, and without any varnished appearance. This film, when wet, will not bear pumping on, but is so rotten that a small stream of water allowed to impinge upon it makes a round hole. The Collodion is non-contractile, and so far from admitting of being pushed backwards and forwards after fixing with the Hyposulphite, it at once breaks away in short pieces under such treatment. Fixing agents will often remove the image from a Collodion of this kind, because the Iodide of Silver is not imprisoned by the Pyroxyline, but lies loosely upon its surface.

Here we repeat the remark before made when speaking of the action of Sulphuric Acid—viz., that the secondary or disintegrating action of Nitric Acid is always greater when the parchmentizing effect has been previously produced; and we may also anticipate an observation to be made a few pages in advance, by adding that one kind of cellulose, such as flax, may be disintegrated by the Nitric Acid more readily than another—viz., cotton.

To secure the full disintegrating action of weak Nitric Acid in the ordinary process of preparing Pyroxyline, the bulk of Nitric Acid present in the Nitro-Sulphuric Acid, should be at least equal to that of the Sulphuric Acid, and may with advantage be many times greater. The cotton will then assume an opaque appearance on being dipped in the mixture, and the Collodion will lack those properties of strength and toughness before referred to.

Composition, by volume, of Nitro-Sulphuric Acid for

preparing Photographic Pyroxyline.—The following table—

	Oil of Vitriol, 1·845 at 60° F.	Pure Nitric Acid, 1·45 at 60° F.	Water.
No. 1	3	1	$\frac{7}{8}$
No. 2	2	1	$\frac{5}{8}$
No. 3	1	1	$\frac{5}{16}$
No. 4	1	2	$\frac{5}{32}$
No. 5	1	3	0

exhibits the composition of five different mixtures of Sulphuric and Nitric Acid, in which an attempt has been made to graduate the proportion of water in such a way that the percentage of Peroxide of Nitrogen imparted to immersed cotton fibre may be nearly the same in each: the table was constructed by simple experiment, taking care in each case to work with the maximum quantity of water, and stopping the addition of water only when it was found that the product left a thick sediment on being dissolved in Ether and Alcohol.

One hundred grains of purified and dried cotton immersed in either of these five mixtures, with the precautions necessary to prevent any loss from solution, ought to weigh one hundred and sixty grains: the Pyroxyline in each case is soluble, to a great extent, in Glacial Acetic Acid, and also in boiling absolute Alcohol; whilst the resulting Collodion does not produce an entirely opaque film (art. PYROXYLINE). A more careful examination seems to indicate that if there be a difference in the strength of the mixtures given in the above table, No. 1 is somewhat stronger than No. 5.* The Collodion however from No. 1 is more fluid than that from No. 5, thus showing that in

* If any one should desire to examine the above acids as regards their strength or power of imparting NO_2 to the fibre of Cotton, let it be borne in mind that in the case of No. 1 the percentage amount of NO_2 in the Pyroxyline will increase considerably if the Cotton be permitted to remain for several hours in the cold acid. The proportion of Nitric Acid in this mixture is so small, being little more than one-fifth of the total bulk, that the Nitric Acid is in a measure *exhausted* in acting upon the fibre, and consequently a rather low substitution body is formed: the Cotton imbibes the liquid like a sponge, and for the first half-hour only those portions of the acid which touch the fibre produce any effect; afterwards, however, a process of diffusion goes on in the liquid, and fresh acid coming into contact with the fibre, more Peroxide of Nitrogen is communicated to it.

addition to high temperature and dilution of the mixture with water, an excess of Sulphuric Acid has to do with flowing properties of Collodion. A greater amount of fluidity than exists even in the Collodion from No. 1 may be produced by dipping the Pyroxyline first in No. 1, to secure the full action of the Sulphuric Acid, and afterwards in No. 5; the weak Nitric Acid will then act more decidedly than it would have done upon a product produced by one immersion.

The temperature employed for the above table of acids may be 150° Fahr.; and, in making the Pyroxyline, we find that the lower numbers give a product which has an opaque appearance; whereas the Pyroxyline made by Nos. 1 and 2 exhibits no opacity. The five samples of Collodion differ very much in the rapidity with which they set upon the glass, and also in their physical structure; the first setting rapidly and producing a horny film: the last scarcely possessing any power of setting. The only way of overcoming this, and putting them on something like a par, is by varying the proportions of Ether and Alcohol in the solvents, using more Alcohol in the former, and more Ether in the latter. Observe, however, that although the lower members of the series in the above table ought to yield a Collodion setting less rapidly upon the glass than the upper members, yet that this observation only applies when the full quantity of water is employed in the Nitro-Sulphuric Acid. For, as before shown, the setting power is injured by a weak Nitric Acid, but not so much by a stronger Acid: hence No. 5 would produce a Collodion with sufficient power of setting if the amount of water in the Nitric Acid were reduced; but in this case the film would possess the objectionable properties of Pyroxyline made in strong acids, being glutinous and difficult to pour.

Effect of Raising the Temperature.—Although we have spoken of fluidity of Collodion, and tenacity of the film as affected by the relative proportions of water, Sulphuric Acid, and Nitric Acid present in the Nitro-

Sulphuric Acid, yet such remarks must be taken very much in connection with the temperature at the time of putting in the Cotton, since the physical modifications produced by the two constituent acids are seen in an exaggerated degree when the Nitro-Sulphuric mixture is *heated*. An acid which gives an insoluble and explosive product in the cold, will yield Pyroxyline perfectly soluble at a higher temperature. Pyroxyline prepared in acids barely warm, makes Collodion which is glutinous and difficult to pour on large glasses, even although containing as little as two or three grains of the soluble Cotton to the ounce. The film soon becomes surface-dry, and repels the developer so that it cannot be made to flow up to the edge: on examination after fixing, it shows cellular spaces and structural lines. *Hot acids*, on the other hand, yield Pyroxyline of the kind which is easily soluble in Ether and Alcohol to the extent of eight or ten grains to the ounce of solvents, and the resulting Collodion is limpid and adherent to the glass. There is also an absence of structural marking in this Collodion, the transparent layer being nearly homogeneous, even when highly magnified.

The reader will perceive that the above physical effects of increased temperature are almost identical with those before attributed to a dilution of the Nitro-Sulphuric Acid with water. This is quite natural, because heat and dilution co-operate in increasing the action of the acids upon the fibre. What we have to do in preparing a Pyroxyline for fluid and adhesive Collodion, is to hit the exact point at which disintegration of the fibre commences, and to add more water, and raise the temperature a few degrees, if after an immersion of five or ten minutes the Pyroxyline appears strong and unyielding, like ordinary cotton.

Different forms of Cellulose.—Cotton, Straw, Pith, Flax, &c., with the manufactured fabrics produced rfom the same, may be converted into soluble Pyroxyline, but the product will be more or less different in each case. When a rather concentrated Nitro-Sulphuric Acid is used, Cotton may give a glutinous Col-

lodion, and Calico a fluid Collodion. In another acid, weaker than the last, the Cotton succeeds well, whilst Calico instantly dissolves. The difference in the two cases appears to depend principally upon the *thickness of the fibre;* Calico produces Pyroxyline of the fluid kind, and is partially dissolved, because the Nitric Acid, in acting on the outside portions of the closely-twisted fibre, is reduced in strength, and hence the interior of the fibre is left more nearly in the condition of Xyloidine. It is possible, also, that with this weakening of the acid there may be a corresponding rise of temperature, which would assist in producing a powdery Pyroxyline, or in causing solution.

Linen, even when selected of the same thickness, yields a more limpid Collodion than Calico, and one of which the film is less tenacious and contractile. These peculiarities cannot be satisfactorily explained, unless they depend upon a difference in *composition;* which is not improbable, since it is known that Flax can be distinguished from Cotton by chemical tests, being more easily discoloured by the action of alkalies.

Both Linen and Calico undergo a change by constant use, which is recognized on making the material into Pyroxyline. Old and rotten rags are quickly disintegrated by the acid mixture, and the Pyroxyline produces a highly structureless Collodion, which adheres with much tenacity to the glass. *Paper* has been at different times much recommended for the preparation of Pyroxyline, but it will easily be gathered from the above remarks that it is an unfit material; for not only do different samples of paper vary greatly in thickness, which, as before shown, would affect the action of the Nitric Acid, but, being made both from Cotton and Linen rags, some of which rags are new, and others old and rotten, they cannot be expected to produce uniformity. The Swedish filtering paper imported into this country for chemical purposes, has been stated to be uniform, but this assertion is not altogether correct; the Pyroxyline being at one time structureless, and at another comparatively glutinous, even with the same Acids.

In addition to the materials mentioned above, others have been tried, such as China Grass, the Pith of the Jerusalem Artichoke, the Fibre of the Aloe, &c., but the result was only to confirm the opinion above expressed, that on each material the Sulphuric Acid, and also the Nitric Acid, produces a different effect. The Fibre of the Grasses, including Flax, appears to be more easily disintegrated and dissolved both by Acids and Alkalies than that of Cotton, and to be convertible into sugar with greater facility.

A point of some importance, as regards the manufacture of Pyroxyline, is the cleansing of the Fibre thoroughly from adhering resinous matter, which, if allowed to remain, deoxidizes a portion of the Nitric Acid, and so far weakens it as to ensure the immediate destruction of a portion of the cellulose at high temperatures. A convenient substance to employ in cleansing is a diluted alkali, which converts the resin into a soap more or less soluble in water. It is probable that the differences which have been said to exist between Cotton of various growths may depend in part upon the presence or absence of this resinous matter. The Manufacturer who wishes to work with great accuracy, and to emply the largest quantity of water possible in the Nitro-Sulphuric Acid, should also bear in mind that Cotton is a hygroscopic substance, and requires to be artificially dried. A minute proportion of moisture present upon the very surface of the Cotton, would produce a greater effect in causing solution than the same quantity of water added to the Nitro-Sulphuric Acid, since it would dilute only that portion of the Acid which touches the Fibre, and thus would cause a rise in the temperature.

Photographic Properties of Various Kinds of Pyroxyline.—In preparing Pyroxyline from the five different mixtures given in the table of composition of Nitro-Sulphuric Acid at page 155, it is found to differ in its Photographic properties as well as in its physical properties. As regards intensity of the Negative image, we observe that Pyroxyline made in the mixtures at

the top of the scale, which contain an excess of the diluted Oil of Vitriol, tends to produce more intense images than Pyroxyline from No. 4 or No. 5, in which the diluted Nitric Acid is in excess. The difference in the two cases is caused by the Oil of Vitriol, since the same effect of increasing intensity can be obtained by parchmentizing the Fibre first, and converting it into Pyroxyline afterwards; and it is not improbable that this action of the Sulphuric Acid in increasing intensity depends upon a conversion of the Cellulose into a substance resembling dextrine in its photographic action.

Irrespective of the proportions of the two Acids, the quantity of water in any mixture of Nitro-Sulphuric Acid will affect the photographic intensity of the resulting Pyroxyline and Collodion. The effect is evidently due to the same action of weak Nitric Acid as that which causes it to disintegrate the Fibre, for if we take a sample of Pyroxyline previously parchmentized by Oil of Vitriol, and capable of yielding great intensity in Collodion, we may destroy its properties in that respect most completely by dipping it for an instant in a warm mixture containing an excess of very weak Nitric Acid. When speaking of the Negative Nitrate Bath, it will be shown that it loses its power of producing a dense picture if a little organic matter oxidized by Nitric Acid be added to it; it appears, therefore, that Nitrate Acid is capable of producing with organic bodies a substance of unknown composition, which is injurious to the intensity of the photographic image. This subject, however, is not at present clearly understood, and we must, therefore, be satisfied with indicating the facts as they stand.

The *temperature* of the Nitro-Sulphuric Acid at the time of immersing the Cotton invariably affects the photographic properties of Pyroxyline. At high temperatures, a portion of the Fibre is converted into a substance which has a bitter taste, and turns brown when treated with Alkalies. This substance is believed to be Nitro-Glucose, formed by the action of strong Nitric Acid upon Grape Sugar: the Grape Sugar itself

being produced from the Cellulose by contact with the warm and diluted Sulphuric Acid. In studying the effect which this bitter product of decomposition is likely to produce, we may prepare Nitro-Glucose, and add it to Collodion. Nitro-Glucose diminishes the sensitiveness of the film to weak rays of light, but increases the rapidity and intensity of the development in Negative pictures. Vigorous images are produced even in a very dull light, but they are always liable to be black and white without middle tints, or to solarize, and become extremely red in the most exposed parts of the film, where the light acts strongly. Collodion made at very high temperatures, although possessed of great fluidity, adhesiveness, and freedom from structural lines, with other physical advantages before enumerated, is found less useful for ordinary work than samples prepared at a lower temperature, and which are not so good in physical properties, being somewhat ropy in hot weather, and drying up more quickly after sensitizing. A film of this latter kind is very sensitive, and every radiation makes a distinct impression even after the shortest exposure.

The author of this Work is inclined to attribute the peculiarities of Collodion made from Linen, or from paper manufactured out of partially decomposed rags, to the presence of Nitro-Glucose in the Pyroxyline. He has found that unless the temperature of the Nitro-Sulphuric Acid be kept low, there is a peculiar disposition to form the bitter resin, not only in Linen Fibre, and partially decayed Cotton Fibre, but also in the pure Cotton Fibre previously converted into vegetable parchment by the action of diluted Sulphuric Acid. In each case the Collodion is highly intense, and when shaken up with Carbonate of Potash assumes an amber-yellow colour, whereas a Pyroxyline nearly free from the bitter matter remains colourless for a time on treating the Collodion with Carbonate of Potash.

It may be proper before leaving this part of our subject to say a few words on an action which *Chlorine* appears to exert in the manufacture of Pyroxyline.

The yellow Nitric Acid of commerce invariably contains a portion of Chlorine, and this is found to exert a decomposing action upon the Fibre, the result of which is to increase the fluidity of the resulting Collodion and also its intensity, but somewhat to diminish its sensitiveness. It is advisable therefore to employ a Nitric Acid from which the Chlorine has been eliminated, since any amount of intensity of Collodion may be obtained by sufficiently increasing the proportion of diluted Oil of Vitriol in the Nitro-Sulphuric Acid, or by raising the temperature, and avoiding the use of too much water in the acids.

In examining commercial samples of Pyroxyline prepared from Cotton-wool, the Writer has met with a variety which gives great intensity of Collodion with an average amount of fluidity. A quantity of Pyroxyline similar to this may be prepared in a mixture of Nitro-Sulphuric Acid containing about two measures of Oil of Vitriol to one measure of Nitric Acid of 1·45 (contaminated with a little Chlorine), and a quantity of water decidedly *less* than that given in the table at page 155. The temperature of the acid mixture must be sufficiently raised to disintegrate the fibre, and so to produce a Pyroxyline which occupies a small space when dry, has rather a yellow aspect, and is inclined to be dusty. The film from the resulting Collodion is not very sensitive, since it contains a notable portion of the bitter resin, but it answers remarkably well for a negative Collodion prepared with a mixed Iodide and Bromide, and its manufacture requires less nicety than the formula which the Author adopts, since the quantity of water in the acids is not so large.

Spontaneous Decomposition in Pyroxyline. — The Author has occasionally failed when using samples of Pyroxyline which have been kept for many months after preparation. A partial liberation of Oxides of Nitrogen appears to take place in some instances, forming an atmosphere of red fumes within the bottle. Pyroxyline which has undergone much decomposition from the use of a very high temperature in the pro-

cess of manufacture may be expected to change in this way, and especially so if the acids are not thoroughly removed by washing; a little Sulphuric Acid left in the Pyroxyline would keep it continually damp, and perfect dryness is essential to the stability of Pyroxyline. From phenomena observed in the decomposition of Nitro-Glucose, it is probable that constant exposure to light favours the change. The products of the spontaneous decomposition of Gun Cotton appear to be the Oxalic Acid and a neutral organic substance having the composition of Gum.

THE PLAIN COLLODION.

The relative proportions of Ether and Alcohol in Collodion affect both the physical and Photographic properties of the solution. This subject has been already alluded to at p. 157, but there are some additional observations to be made.

The use of an excess of Alcohol is advantageous in preventing the Ether from evaporating quickly in hot weather. At temperatures of 90° and 100° Fahr. it is almost impossible, with Collodion containing but little Alcohol, to coat a large glass and immerse it in the Bath before the upper part becomes dry; consequently an uneven coating of Iodide is produced, with a blueness at the top edge. This happens especially when the Spirits are very strong and almost free from water. Another advantage of making Collodion with a large quantity of Alcohol is, that it is more readily wetted by the Bath solution, and does not throw the liquid into greasy lines upon the surface of the film. There is however a practical limit to the use of Alcohol, inasmuch as not being a complete solvent of Pyroxyline it alters the structure of the film, rendering it gelatinous.

The quality of the Pyroxyline is the first important point to be considered in determining the relative proportions of Ether and Alcohol. With a sample of Pyroxyline made at a low temperature and in rather strong Nitro-Sulphuric Acid containing a minimum of

Sulphuric Acid, barely enough Alcohol should be used in the *plain* Collodion to confer the requisite solubility —viz., an eighth or a twelfth part, by bulk, of the Ether; otherwise the iodized* Collodion will be very tender and easily torn, glutinous and difficult to pour, loosely adherent to the glass, and full of crapy lines and structural markings.

Pyroxyline prepared from Cotton-wool by the formula with a large excess of Oil of Vitriol will bear more Alcohol than the last, and with some advantage, for the contractility which makes it separate from the edges of the glass is lessened by the addition of Alcohol. The tendency to set quickly and produce water-markings at the upper edge of the plate is also to a great extent obviated, as is also the rapid surface-drying of the film after taking it from the Bath, which causes it to repel the developer, as before shown. The film, being nearly structureless and very tough, will bear a quantity of Spirits which in other cases would produce crapy lines and tenderness. If the Pyroxyline of this formula be made in acids containing the largest possible quantity of water, the proportion of Alcohol in the plain Collodion may be one-half of the Ether, which will give, after iodizing, equal bulks of the two Solvents; but if the Nitro-Sulphuric Acid was made with less water, then the proportion of Alcohol in the plain Collodion must not exceed *one-third* of the Ether, or the film will be woolly at the lower corner of the plate.

It will be found that the solubility of this tough kind of Pyroxyline is *increased* by employing the maximum quantity of Alcohol, so that if the plain Collodion be diluted with Ether, a precipitate will take place. With other kinds of Pyroxyline differently prepared, the addition of Ether to the plain Collodion produces no precipitate.

In the case of Pyroxyline prepared in Nitro-

* This observation supposes the plain Collodion and the iodizing compound to be kept in separate solutions; two measures of the latter being added to six measures of the former.

Sulphuric Acid containing equal bulks of Oil of Vitriol and Nitric Acid, with the maximum of water, it is advisable to reduce the quantity of Alcohol somewhat; for if too much Alcohol be employed, the *setting* of the Pyroxyline will be so greatly retarded that the upper edge of the film will become dry before the lower part has solidified sufficiently to take the Bath without precipitation of the Pyroxyline. Such an effect could could not happen in the case of the first formula of page 155, containing Oil of Vitriol in excess, because it would be impossible to use such a mixture in a state sufficiently weak to destroy the property of setting in the resulting Pyroxyline: before that point was reached the cotton would dissolve in the acid.

The exact *strength* of the Alcohol used in Photography must always be noted, since the effect of water when present in any quantity is to produce viscidity of Collodion, and more rapid decomposition under the influence of the iodizing compound. The experience of Photographers is favourable to the employment of even a stronger spirit than that usually recommended; and when it can be obtained, the Alcohol of ·805 at 60° Fahr., sold in commerce as absolute, may be preferred, as a rule.

With the most horny kind of Pyroxyline, however, prepared by the first formula of page 155, a little water appears necessary, to open out the structure of the film and prevent it from assuming a condition in which it resembles Gutta Percha in being impervious to liquids; but in the case of Pyroxyline from formula No. 3, of page 155, such as is recommended for Positives, the film will be sufficiently porous, even with the whole of the Alcohol in the absolute state. With formula No. 1 the Alcohol of ·805 may also be employed, if the proportion be increased until it nearly doubles that of the Ether.

Photographic Effects of Excess of Alcohol in Collodion.—The addition of Alcohol to Collodion lessens the contractility of the film, and renders it soft

and gelatinous. These conditions are favourable to sensitiveness, perhaps from the play of affinities being promoted by the loose manner in which the particles of Iodide are held together. The extra sensitiveness obtained by use of Alcohol, however, does not increase after a certain point; on the contrary, it diminishes, for it appears to be necessary to extreme sensitiveness that the film should coagulate within a certain time after it has been coated, and therefore the addition of Alcohol must be stopped when the film loses its ready setting qualities, and is not coherent under the finger. Hence a porous Collodion is soon injured in sensitiveness on adding too much Alcohol, but a strong and tough Pyroxyline will bear equal bulks of the two Solvents without loss in that respect.

The above observation as to the effect of excess of Alcohol in diminishing the sensitiveness of the film to dark objects applies particularly when the atmosphere is cold and damp, and evaporation is retarded. At a very high temperature and in a dry air it does not apply, since the presence of Alcohol is then useful in preventing the film from becoming surface-dry, especially when it is necessary to keep the sensitive plate for a long time between exposure and development.

Intensity of Negative is much favoured by using a full quantity of Alcohol, and particularly when large glasses are coated, and long focus lenses, which work slowly, are employed. The difference is doubtless due in part to the structure of the film being opened out by the Alcohol, so as to assist the developer in penetrating, and partly to the rapidity of evaporation and consequent surface-drying being diminished. Hence in hot weather the Alcohol acts very beneficially, and with Collodion made almost entirely of Ether, the Negatives are unusually weak at such times. Pyroxyline of the horny kind is especially liable to lose intensity at high temperature unless the Alcohol be added freely so as to prevent the film from becoming hard and impervious.

Decomposition of Plain Collodion by Keeping.—Plain Collodion tends to become more liquid by keeping, and often acquires the property of eliminating Iodine rapidly from the iodizer; but the rapidity with which the change takes place, varies much with the mode of preparing the Pyroxyline and with the quality of the Ether. Supposing all the materials to be pure, the decomposition after keeping for several months in a cool and dark place is very slight, and is generally considered to improve the quality of the Negative rather than otherwise: it imparts a slightly red or purple tone to the image, without much affecting the sensitiveness, and hence many prefer to keep a stock of Collodion always on hand, that it may settle down clear, and "ripen." This proceeding, however, would be very far from safe with an unstable Pyroxyline, or an inferior Ether, since the Oxides of Nitrogen would then be set free from the Gun Cotton, and injury to the sensitiveness would result from elimination of Iodine after iodizing.

When great stability is an object, as in exporting Collodion to foreign climates, the Pyroxyline ought not to be made in such a way as to produce much *decomposition* in the Nitro-Sulphuric Acid. For instance, if we take pieces of old linen and immerse them at a temperature of 150° Fahrenheit in a Nitro-Sulphuric Acid made purposely very weak, the greater part will dissolve, but a few fragments remain, which, when washed and applied to the tongue, have a bitter taste. In this case the Pyroxyline is partially decomposed in the Acid, and Collodion made from the product might work well at first, but after keeping for twelve months in the plain state would probably be as thin as water, and produce a rotten and insensitive film.

The best kind of Pyroxyline for yielding a stable Collodion, according to the Author's experience, is that made from Cotton-wool, and at rather a low temperature. This preparation has been proved to retain

its original properties *nearly* unchanged for nine months. The test for decomposition of Pyroxyline is *agitation of the Collodion with dry Carbonate of Potash.* When so treated it should remain colourless for a certain time: if it assume a brown tint in less than two hours, traces of the compound above named as resembling Nitro-Glucose are present.

Plain Collodion, made at a temperature of 170° to 180° Fahr., will keep well for a few weeks, but when exported to a distant climate, and subjected to an elevated temperature, it liberates Iodine from Iodide of Potassium somewhat quickly, and is useful only for taking Positives, or Negative views when shortness of exposure is not an object. Carbonate of Potash shaken up with this kind of Collodion strikes a brown colour.

A point which should not be overlooked in preparing Collodion for keeping is the length of time during which the fibre of the Cellulose remains in the Nitro-Sulphuric Acid. A short immersion (five minutes) is the best, but if the material be left for half an hour or longer, as may sometimes be done without solution taking place, the Collodion will often acquire by degrees the property of striking a brown colour with Iodide of Potassium.

The quality of the *Ether* is very important in making a Collodion of uniform properties. It is possible to obtain an Ether which will remain for months without assuming the condition known as "ozonized," in which it liberates Iodine from Iodide of Potassium; but Ether containing Aldehyde or organic impurity will soon change.

The Photographer will be guided partly by the quality of his Ether in deciding as to the best formula for a Pyroxyline, because an inferior Ether soon renders the Collodion rather limpid through formation of Acetic Ether or some similar product, by which the setting power of the Pyroxyline is diminished. It must also be borne in mind that when this impure

Ether liberates Iodine in the Iodized Collodion, a corresponding portion of the alkali Potash is set free, which, as we shall presently show, adds to the limpidity, and lessens the setting powers. To meet this difficulty, the Pyroxyline should be made slightly more tough and contractile than is necessary, which may be effected by reducing the temperature of the Acid a few degrees. Also, since impure Ether soon becomes ozonized, a high temperature of Nitro-Sulphuric Acid ought to be avoided, as likely to render the Pyroxyline unstable.

Inferior Ether usually produces a more intense Collodion than pure Ether, but the plain Collodion does not keep for any length of time without change, soon losing its sensitiveness, and yielding pictures which are black and white without middle tints. A rapid elimination of Iodine takes place on adding the iodizer, and the film is weak and rotten. In some cases, commercial Ether is contaminated with organic Oils having a foul smell, or contains traces of the Alkali employed in the processes of purification. The latter impurity is particularly objectionable, because Alkalies and Carbonated Alkalies decompose Collodion, rendering it limpid, and destroying the setting properties. "Methylated Ether" (see the Vocabulary), is largely employed in the manufacture of Collodion, but where expense is not an object, the Writer recommends the pure Ether in preference. (Read the article ETHER, in the Vocabulary, for further particulars.)

IODIZING SOLUTION.

Different Iodides vary in their effect upon plain Collodion. Those which have an acid reaction, like the Iodide of Cadmium, may be expected to increase the glutinosity. But Alkaline Iodides, such as Iodide of Potassium or Ammonium, render it limpid and structureless. Fixed Alkalies or Alkaline Carbonates have a more marked effect than Alkaline Iodides, as may be shown by agitating plain Collodion with pow-

dered Carbonate of Potash: in the course of a few days it becomes as fluid as water. The first effect of the Alkali, however, upon Pyroxyline, made by the formula with excess of Oil of Vitriol, is to render the Collodion *glairy*, so that the bottle may often be completely inverted without any immediate loss. The same observation applies to Alkaline Iodides: they thicken the Collodion slightly in the first instance, and afterwards render it more limpid. When Collodion gradually becomes limpid under the action of an Alkaline Iodide, it loses its power of setting upon the glass; but there is a remarkable difference between Collodions in the rapidity of this change, and those which are tough and unyielding when newly made withstand the action of the Alkali for a much longer time.

The reader will perceive that the effects now attributed to the action of alkaline Iodides upon Collodion—viz., limpidity and a diminished power of setting, are the same as those spoken of under the head of dilution of the Nitro-Sulphuric Acid with water. There is, however, this important difference in the two cases, that in the former an increase of photographic intensity accompanies the porosity, but in the latter the intensity is diminished, as already shown.

Iodide of Cadmium.—The stability of this compound is its great recommendation: Ether, unless highly ozonized, has little or no effect in liberating Iodine from it. Another advantage of the Iodide of Cadmium is, that it does not destroy the setting properties of the Pyroxyline as the alkaline Iodides eventually do.

The Collodion should be prepared purposely when Iodide of Cadmium is used as an iodizer. Collodion containing Pyroxyline made at a low temperature and in rather strong acids, works tolerably well after iodizing with the Potassium or Ammonium compound, and keeping until liberation of Iodine and liquefaction have taken place: but with Iodide of Cadmium it would be in every respect unsatisfactory, flowing in a slimy manner upon the plate, exhibiting crapy lines,

repelling the developer, and splitting away from the glass on drying. When the Pyroxyline is made in strong acids at a very high temperature, the Collodion is often sufficiently fluid, but yet is not altogether adapted for iodizing with the Cadmium Salt, from its tendency to produce "woolliness" or unevenness of film at the lower edge of the plate. The proper kind is that prepared in weak acids, and sufficiently parchmentized by the Oil of Vitriol to give the requisite degree of intensity.

Iodide of Potassium.—This Salt is well adapted for iodizing Collodion not required to possess keeping properties, but its sparing solubility in Alcohol and Ether is an objection. Collodion containing $4\frac{1}{2}$ parts of Ether of ·725 to $3\frac{1}{2}$ of Alcohol ·816, will carry nearly three grains of Iodide of Potassium to the ounce. With equal bulks of Ether and Alcohol the full quantity—viz., four grains, may be dissolved. Five parts of Ether with three of Alcohol will not take more than 2 or $2\frac{1}{4}$ grains to the ounce. The admixture of Iodide of Cadmium with Iodide of Potassium increases the solubility of the latter Salt, by forming a double Salt, the Iodide of Potassium and Cadmium. To produce this compound, which is well fitted for iodizing Collodion containing five parts Ether to three of Alcohol of ·816, equal weights of the two Iodides may be taken. These proportions are not strictly correct, but they are sufficiently near for practical purposes.

It may also be remarked that the quantity of an alkaline Iodide which any Collodion will carry depends partly upon the Pyroxyline. With that particular kind of Pyroxyline which is recommended for Negatives in this Work, no more than $3\frac{1}{2}$ grains per ounce must be employed, otherwise the Iodide of Silver will be precipitated upon the *surface* of the film at the lower edge, and marks will result. By mixing the Iodide of Potassium with Iodide of Cadmium, or by using Iodide of Cadmium alone, a larger quantity of Iodide may be used without the appearance of markings.

The effect of using an iodizing solution containing more Iodide of Potassium than the Collodion will retain in solution, is not always to produce an immediate precipitation, such as would result if the Pyroxyline were omitted, and the iodizing solution added to an equivalent quantity of Ether and Alcohol. The presence of the Pyroxyline prevents a visible deposition, but the Collodion will produce a spotted image, and, after standing for some days, crystals will form upon the sides of the bottle.

When the whole of the Alcohol contained in the Collodion is of the strength of ·805, commercially known as "absolute," it will scarcely be safe to iodize with Iodide of Potassium only, unless the proportion of Alcohol is nearly double that of the Ether; much, however, will depend upon the degree of dryness of the Ether itself, since the commercial Ether often contains Water dissolved in it, in sufficient quantity to prevent the precipitation of the Iodide of Potassium. The preparation of an iodizing solution of Iodide of Potassium is a troublesome process with Alcohol of ·805, since it is necessary to pulverize the Iodide very carefully, and to boil the spirit upon it; in cold weather, such an iodizer is apt to deposit cubical crystals upon the sides of the bottle containing it.

Commercial Iodide of Potassium is often contaminated with Carbonate of Potash. This Salt has an injurious action, not only in throwing a white deposit of Carbonate of Cadmium when the mixed Iodides are used, but also in reacting upon the Collodion, and producing rapid liquefaction, as before shown. Pure Iodide of Potassium is now prepared purposely for Photography; the crystals have a slightly yellow tint, and the Alcoholic solution liberates Iodine slowly on exposure to Light.

Iodide of Ammonium is useful in iodizing Collodion, when it is required to add also a portion of Bromide; if any Iodide of *Potassium* were present in such a case, a white deposit would form, on account of the sparing

solubility of Bromide of Potassium in Spirits free from water. Collodion containing $4\frac{1}{2}$ drachms of Ether to $3\frac{1}{2}$ of Alcohol ·816, will not carry more than a quarter of a grain of Bromide of Potassium to the ounce, but it will easily dissolve a much larger quantity of Bromide of Ammonium or Bromide of Cadmium. The only objection to the use of Iodide of Ammonium is its instability, and the difficulty of invariably obtaining it in a pure state, the Writer having found that most of the samples prepared by aid of Sulphuretted Hydrogen or Hydrosulphate of Ammonia, contain traces of a Sulphur compound, and are inferior to those made in the moist way, by precipitation. When Iodide of Ammonium becomes brown by keeping, it may be decolorized by shaking it up in a bottle with a little Ether, and drying upon blotting paper.

Iodide of Sodium is intermediate in solubility between Iodide of Potassium and Iodide of Ammonium, and would be a valuable compound for iodizing if it could be obtained commercially in a pure state.

Iodide of Iron was formerly used in Photography, but has now become obsolete. It produces a very sensitive Collodion at first, but soon reacts upon the Pyroxyline, and the Collodion becomes reduced to the condition of a jelly. The Nitrate Bath is also thrown out of order, Protonitrate of Iron being formed, which precipitates Metallic Silver on the sides of the trough.

Chemical and Photographic Action of the various Iodides in Collodion.—With recently iodized Collodion the difference in sensitiveness between the various Iodides is not very marked if they are in a pure state. The presence of Carbonate of Potash, Iodate of Potash, or Chloride of Potassium in the commercial Iodide of Potassium at once diminishes the sensitiveness; and any trace of a Sulphur compound in the Iodide of Ammonium will have the same effect.

The *intensity* of Negative Collodion does not vary materially with the Iodide, if the Collodion be tested soon after iodizing. Nevertheless by close observation

minute differences can be detected, and Iodide of Potassium will be found to give a somewhat more vigorous picture than Iodide of Ammonium. With any Iodide also the intensity will be lessened by adding too large a quantity of the Iodide, and especially when the setting power of the Collodion is small. If, from any cause, such as excess of Iodide, deficiency of setting power in the Collodion, &c., the sensitive film of Iodide be allowed to lie loosely upon the surface of the Collodion, the picture will be very feeble, and will often fall away when the fixing agent is applied.

After Collodion has been kept for a time in the iodized state, both the sensitiveness and the intensity will vary with the Iodide chosen, because, as before shown, an affinity exists between the Pyroxyline and the base of the Iodides. Alkaline Iodides are soon decomposed by Collodion, and hence a loss of sensitiveness, depending partly upon the retarding effect of free Iodine and partly upon the new compound formed by the liberated Alkali. The liquefaction of the Collodion, and its diminished power of setting upon the glass, must also be supposed to be injurious to sensitiveness. The *intensity*, however, will increase in consequence of these changes, since free Iodine, although it lessens intensity in a dull light, tends to prevent feebleness of the image from solarization in a strong light; and the compound formed by the trace of liberated Alkali, whatever be its nature, has a direct action in adding to the intensity. The liquefaction of the Collodion is also serviceable up to a certain point, by removing the impermeability to the developer which the more dense and horny kinds of Collodion exhibit.

Iodide of Cadmium is the most stable of all the Iodides, yet with Iodide of Cadmium as an iodizer, an amount of change sufficient to lessen the sensitiveness of the Collodion to very dark objects eventually takes place, and with an unstable Pyroxyline or impure Ether, this change may be evident even in a few weeks. Iodide of Cadmium also increases the intensity of

Collodion after a long keeping, especially with Pyroxyline made in rather strong acids. In such a case the Collodion gradually becomes slightly gelatinous, the film solarizing strongly in the parts most acted on by the Light, and the image exhibiting a bright red colour, when viewed by transmission. This state of Collodion is well fitted for photographing in a dull light.

The nature of the Pyroxyline must also be taken into account in estimating the probable effect of iodizing with an Alkaline Iodide. If it has undergone decomposition in the manufacture, the sensitiveness of the Collodion will soon be lost; but if prepared at low temperatures, it remains for a long time unchanged: of all kinds of Pyroxyline the least stable after iodizing is that prepared from Linen in weak acids and at a high temperature.

A point which affects the keeping qualities of a Collodion, or its stability after iodizing, is the presence of *Bromide* combined with the Iodide. Collodion so made assumes the usual yellow tint when mixed with the iodizing solution; but in the course of some hours either the whole or a part of the free Iodine appears to be re-absorbed. This change takes place most rapidly in the case of methylated Ether, but it may be seen more or less even with pure Ether and pure Alcohol. No satisfactory explanation can be given.

To facilitate the comprehension of the decompositions which take place in iodized Collodion, let the following experiments be made. Take Nitro-Glucose and add it in small quantity to ordinary Collodion iodized with the Potassium compound: the elimination of Iodine will be somewhat more rapid than usual, the Collodion at the same time losing sensitiveness and gaining intensity. Next dissolve Nitro-Glucose in Spirits of Wine, and boil it in a test-tube with powdered Carbonate of Potash: the liquid becomes brown, and evolves a smell of burnt sugar: a few drops of it in iodized Collodion rapidly destroy the sensitiveness but add much to the blackness of the Negative. In a third

experiment introduce a portion of a reducing agent, such as grape-sugar, into iodized Collodion: the result will be to lessen the sensitiveness on keeping, and to increase the intensity. The experiment last described shows that not only the nature of the particular Iodide, and that of the Pyroxyline, but also the presence of foreign organic substances may affect the keeping properties of iodized Collodion; hence the importance of using Ether which has been carefully freed from traces of Aldehyde, &c., since even the employment of an Iodide as stable as that of Cadmium will not prevent decomposition if substances are present in the Collodion which have an affinity for Oxygen.

Another experiment, illustrating the effect of changes in Collodion after Iodizing, is the following:—Take Nitrate of Soda, and boil with it Alcohol of ·805 until a saturated solution has been obtained: a few minims of the liquid, added to an ounce of iodized Collodion, will increase the intensity. A nitrate is one of the products of decomposition of Collodion by alkalies or alkaline Iodides, and may sometimes be seen in the form of well-defined crystals at the bottom of the bottle.

CHAPTER VII.

THE CHEMISTRY OF THE NITRATE BATH.

THE solution of Nitrate of Silver in which the plate coated with Iodized Collodion is dipped, to form the layer of Iodide of Silver, is known technically as *the Nitrate Bath*. The Chemistry of Nitrate of Silver has been explained at page 108, but there are some points relating to the properties of its aqueous solution which require a further notice.

Solubility of Iodide of Silver in the Nitrate Bath.—Aqueous solution of Nitrate of Silver may be mentioned in the list of solvents of Iodide of Silver. The proportion dissolved is in all cases small, but it increases with the *strength* of the solution. If no attention were paid to this point, and the precaution of previously saturating the Nitrate Bath with Iodide of Silver neglected, Iodide of Silver in the film would be dissolved when left too long in the liquid.

This solvent power of Nitrate of Silver on the Iodide is well shown by taking the excited Collodion plate out of the Bath, and allowing it to dry spontaneously. The layer of Nitrate on the surface, becoming concentrated by evaporation, dissolves the Iodide and produces a transparent, spotted appearance.

In the solution of Iodide of Silver by Nitrate of Silver a *double salt* is formed, which corresponds in properties to the double Iodide of Potassium and Silver in being *decomposed* by the addition of water. Consequently, in order to saturate a Bath with Iodide of Silver it is only necessary to dissolve the total weight of Nitrate of Silver in a small bulk of water, and to add to it a few grains of an Iodide; perfect solution takes

place, and on subsequent dilution with the full amount of water, the excess of Iodide of Silver is precipitated in the form of a milky deposit.

The above-named double salt of Iodide of Silver and Nitrate of Silver has been termed by Schnauss the "Iodo-Nitrate of Silver;" and although in the Collodion Nitrate Bath it is present only in small quantities, and in a state of solution, it is quite possible to obtain it in well-defined crystals. No corresponding compounds containing Bromide and Chloride of Silver are known, and hence it will not be necessary to saturate the Bath with those salts when it is desired to use them in Collodion.

Although the addition of water to the Negative Bath renders it milky by precipitation of Iodide of Silver, dilution with Alcohol has not the same effect.

Acid condition of Nitrate of Silver.—A solution of Nitrate of Silver prepared from the commercial Nitrate has usually an acid reaction; the crystals having been imperfectly drained from the acid mother-liquor in which they were formed. Hence, in making a new Bath it is advisable not only to saturate it with Iodide of Silver, but to neutralize the free Nitric Acid it contains.

The quantity of this Acid is very variable. If the Nitrate has been carefully dried at 240° Fahrenheit, and then crystallized a second time, no Nitric Acid can be detected, the concentrated aqueous solution slowly restoring the blue colour of reddened Litmus. This alkaline effect upon reddened Litmus the Writer believes to be the proper reaction of pure Nitrate of Silver, since he finds it to exist in samples of Nitrate which have never undergone fusion. On the other hand, Nitrate of Silver which has been crystallized only once from the acid mother-liquor, without any attempt at careful drying, is often so decidedly acid that it cannot be employed for the Bath until neutralized.

The Nitrate Bath, although perfectly neutral when first prepared, may become acid by continued use, if

Collodion containing much *free Iodine* be constantly employed. In that case a portion of Nitric Acid is liberated, and Iodate and Iodide of Silver are formed.

If the Bath contains *Acetate* of Silver, free Iodine liberates Acetic Acid in place of Nitric Acid; and Nitric Acid added to such a Bath neutralizes itself and displaces Acetic Acid.

The actual quantity of acid liberated by Collodion which has become brown from decomposition, is very inconsiderable, and it is quite a mistake to be continually neutralizing the Nitrate Bath. When, however, the trough which holds the Bath is narrow, and the plates large, a minute addition of alkali may occasionally be required, to prevent the film from losing sensitiveness, and yielding weak metallic Negatives.

Alkaline condition of the Bath.—By "alkalinity" of the Bath is meant a condition in which the blue tint is restored to reddened litmus-paper. This change, when rapid, indicates that a free Oxide is present in solution, which by combining with the acid in the reddened paper neutralizes it and removes the red colour.

If a small portion of caustic Potash or Ammonia be added to a strong solution of Nitrate of Silver, it produces a brown precipitate, which is Oxide of Silver. The solution, however, from which the precipitate has separated, is not left in a neutral state, but possesses a distinct alkaline reaction, since Oxide of Silver is sparingly soluble in water, and the solution restores the blue colour of reddened Litmus. Both Oxide of Silver and Carbonate of Silver are also *abundantly* soluble in water containing Nitrate of Ammonia; which salt is continually accumulating in the Bath when compounds of Ammonium are used for for iodizing.

An alkaline Bath is fatal to success in Photography, producing that universal darkening of the film on applying the developer to which the name of "fogging" has been given. Hence care must be used in adding to the Bath substances which tend to make it alkaline. Collodion containing free Ammonia, often sold in

the shops, gradually does so. The use of Potash or Carbonate of Soda to neutralize the Bath, or even of Chalk or Marble, if Salts of Ammonia are present, has the same effect, when an excess is employed; and hence a trace of Acetic or Nitric Acid must afterwards be added.

The mode of testing a Bath for alkalinity is as follows:—a strip of porous blue litmus-paper is taken and held to the mouth of a bottle of Glacial Acetic Acid until it becomes reddened; it is then placed in the liquid to be examined and left for ten minutes or a quarter of an hour. If free Oxide of Silver be present in solution, the original blue colour of the paper will be gradually restored. This experiment must not be made in a strong light, or the litmus-paper will darken, and the blue colour be obscured. Indeed it is always somewhat difficult to examine a Nitrate Bath by test papers, since the pure Nitrate of Silver has a slightly alkaline reaction; and hence the Photographic effect of alkalinity—viz., cloudiness of the image, will to the amateur afford a more certain guide. The Writer believes that the use of *Ammonia* for the purpose of neutralizing the Bath is the most common cause of failure from alkalinity, few being aware that *a single drop of strong Ammonia* will neutralize a comparatively large quantity of acid.

Acetate of Silver in the Nitrate Bath.—In preparing a new Bath, if the crystals of Nitrate of Silver are acid, it is usual to add an alkali in small quantity. This removes the Nitric Acid, but leaves the solution faintly alkaline from Oxide of Silver. If Acetic or Nitric Acid is then dropped in, it forms Acetate or Nitrate of Silver by combination with the Oxide.

Acetate of Silver is not formed by the simple addition of Acetic Acid to the Bath, because its production under such circumstance would imply the liberation of Nitric Acid; but if an alkali be present to neutralize the Nitric Acid, then the double decomposition takes place, thus—

Acetate of Soda + Nitrate of Silver
=Acetate of Silver + Nitrate of Soda.

Acetate of Silver is a white flaky salt, sparingly soluble in water. It dissolves in the Bath only in small proportion, but yet sufficiently to affect the Photographic properties of the sensitive Collodion film. The observance of the following simple rules will obviate its production in injurious quantity:—First, when it is required to remove free Nitric Acid from a Bath *not containing Acetic Acid* a solution of Potash or Carbonate of Soda may be dropped in freely; but the liquid must be filtered before adding any Acetic Acid, otherwise the brown deposit of Oxide of Silver will be taken up by the Acetic Acid, and the Bath will be charged with Acetate of Silver. Secondly, in dealing with a Bath containing both Nitric and Acetic Acid, employ an alkali *much diluted* (Liquor Ammoniæ with 10 parts of Water), and add a single drop at a time, coating and trying a plate between each addition; the Nitric Acid will neutralize itself before the Acetic, and with care there will be no formation of Acetate of Silver in quantity.

The question is sometimes asked, how Acetic Acid may be removed from the Nitrate Bath, and Nitric Acid substituted? This operation is somewhat difficult to effect. Nitric Acid, when present in excess, can be neutralized and converted into a *Nitrate*, which is nearly or quite inert in Photography; but to neutralize Acetic Acid is to form an *Acetate*, which is not inert; and the subsequent addition of Nitric Acid to such a solution again liberates Acetic Acid. Evaporation to dryness with a little Nitric Acid is the only means of effectually eliminating the Acetic Acid from the Bath.

Organic Matter in the Nitrate Bath.—Nitrate of Silver has an affinity for certain kinds of organic matter, and when such substances are present, the Photographic action of the Bath is in some way interfered with.

Commercial crystallized Nitrate of Silver is frequently contaminated with traces of an impurity, which is probably produced by organic matters falling into the Nitric Acid employed in dissolving the Silver. Repeated recrystallization is required to remove this substance. If allowed to remain, it injures the sensitiveness of the film to feeble radiations, makes the Negative weak and metallic, reverses the action of the light, and produces either fogging or markings of various kinds, the result of irregular reduction of Silver.

Solutions of Nitrate of Silver often acquire organic contamination by being kept in troughs of Gutta-percha. Pure Gutta-percha seems to have little action upon Nitrate of Silver, but the commercial article is invariably impure. Caoutchouc seems also to be without action, but Caoutchouc vulcanized with Sulphur, such as is used for the tops of watertight baths, will decompose the Nitrate of Silver by degrees. Baths injured by impure Gutta-percha produce fogging of the film, streaks of irregular development, and quick discoloration of the solution of Pyrogallic Acid, attended with variations in the density of the Negative picture.

Albumen and Gelatine soon decompose Nitrate of Silver, and hence the dipping of a few dry albuminized plates, or the floating of chloride-papers intended for the printing process, upon a Collodion Bath, would effectually disorder it, and almost certainly give rise to fogging.

Alcohol and Ether react very slowly upon solution of Nitrate of Silver, and Pyroxyline is almost without effect. Hence when *pure* Collodion is employed, the bath may be kept for many months without much appreciable change. It should however be carefully excluded from light, or the sides of the bottle will be covered with a delicate layer of reduced Silver. Methylated Spirit of Wine is seldom sufficiently free from volatile oil to remain long in the bath without producing partial reduction.

Collodion containing common Rosin, has been recommended for use in the dry Collodion process; but the Rosin finds its way into the bath, and spoils it for the wet process, soon producing solarization of the most exposed parts of the plate, and altering the appearance of the film of Iodide, so that it becomes pale and blue, instead of being yellow and creamy.

The effect produced by organic matters in the bath will be more intelligible if we explain that not only Nitrate of Silver, but also *Iodide of Silver* has an affinity for a certain class of these bodies. Hence when a Collodion film is dipped in a bath of the kind described, a trace of organic matter is carried down and retained in the film. This applies especially to *Albumen*, which has so decided an affinity for Iodide of Silver, that its presence will entirely alter the colour of the film, and render it blue and transparent. A state of bath, in which the Collodion film, instead of being yellow and creamy, appears blue or opalescent, may be produced by organic matter, as well as by a deficiency of Nitrate of Silver.

To remove organic matter from the bath, the following plan is often employed. The solution, having been rendered slightly alkaline by a solution of bicarbonate of Soda or by Ammonia, is exposed for two or three days to a bright sunlight in a transparent bottle, when the greater part of the organic compound separates in combination with the Oxide of Silver. This mode is generally successful in restoring a Bromo-iodized Collodion bath to a good working condition, but often fails in rendering it useful for a simply Iodized Collodion and Pyrogallic developer.

Use of Fused Nitrate of Silver for the Bath.—Fusion has been resorted to with a view of expelling traces of Nitric Acid from the crystallized Nitrate of Silver, and thus lessening the trouble of preparing the bath. It must be observed, however, that decomposition of the Nitrate is liable to occur in melting, *if the crystals are not chemically pure.* A trace of any organic substance,

such as a bit of cork or a fragment of gelatine, adhering to the sides of the porcelain dish, would at the melting point of Nitrate of Silver remove Oxygen, and produce *Nitrite of Silver:* a safer plan is therefore to pulverize the Nitrate and dry it in a hot-air bath, at about twenty degrees above the temperature of boiling water. Supposing the Nitrate to be absolutely free from organic matter, there would be no danger of forming Nitrite in the process of fusion, since the temperature at which Nitrate of Silver decomposes is far above its melting-point.

Nitrate of Silver which has been much decomposed in melting, produces a great peculiarity of development. In the Positive glass process the whites are often solarized, and appear blue by reflected light; whilst in the Negative process the image is highly intense, with over-action in parts like the sky, and the film usually fogs slightly towards the end of the development: on applying the developer the whole picture starts out instantly, and the solution of Pyrogallic Acid becomes muddy instead of assuming by degrees the colour of sherry wine. These effects are not unlike those previously described as due to certain kinds of organic matter in the bath, the reduction of Silver by the developer being in both cases facilitated.

CHAPTER VIII.

ON POSITIVE AND NEGATIVE COLLODION PHOTOGRAPHS.

We use the terms "Positive" and "Negative" so frequently in Photography to denote different kinds of chemicals and pictures, that it is important for the student to have a clear understanding of the meaning of these terms.

A Positive photograph may be defined to be a picture which gives a natural representation of the lights and shadows of an object as seen by the eye.

A Negative photograph, on the other hand, has the lights and shadows *reversed*, so that the appearance of the object is changed or *negatived*.

The following diagrams will serve to make this obvious :—

Fig. 5. Fig. 6. Fig. 7.



Fig. 5 is an opaque image drawn on a transparent ground; fig. 6. represents the effect produced by placing it in contact with a layer of sensitive Chloride of Silver and exposing to light; and fig. 7 is the result of again copying this Negative on Chloride of Silver.

Fig. 7 therefore is a Positive copy of fig. 5 obtained by means of a Negative. By the first operation, the

lights are reversed; by the second, being again reversed they are made to correspond with the original; hence the possession of a Negative enables us to obtain Positive copies of the objects, indefinite in number and all precisely similar in appearance.

The same Photograph may often be made to show either as a Positive or a Negative. For instance, supposing a piece of silver leaf to be cut into the shape of a cross and pasted on a square of glass, the appearance presented by it would vary according to the way in which it is viewed.

Fig. 8.



Fig. 9.



Fig. 8 represents it placed on a piece of black velvet; fig. 9 as held up to the light and viewed by transmitted light.

Positives therefore should be viewed by *reflected* and Negatives by transmitted light.

All Photographs, however, cannot be made to represent both Positives and Negatives. In order to possess this capability it is necessary that a part of the image should be transparent and the other opaque, but with a bright surface. These conditions are fulfilled when an image on Collodion is developed by a reducing agent.

Every Collodion picture on glass is to a certain extent both Negative and Positive, and hence the processes for obtaining both varieties of Photographs are in most respects the same. The conditions of success will be fully described in suceeding chapters. All that refers

to obtaining Positives on Silver-chlorized paper will be treated of under the head of "Positive Printing."

With these preliminary remarks, we are prepared to investigate more closely the *rationale* of the processes for obtaining Collodion Positives and Negatives.

SECTION I.

On Collodion Positives, or Ferrotypes.

Collodion Positives are sometimes termed *direct*, because obtained by a single operation. The Chloride of Silver *acted upon by light alone*, is not adapted to yield direct Positives, the reduced surface being dark and incapable of representing the lights of a picture. Hence a developing agent is necessarily employed, and the Iodide of Silver substituted for the Chloride, as being a more sensitive preparation. Collodion Positives are closely allied in their nature to Daguerreotypes. The difference between the two consists principally in the surface used to sustain the sensitive layer, and the nature of the substance by which the invisible image is developed.

In a Collodion Positive the lights are formed by a bright surface of reduced Silver, and the shadows by a black background showing through the transparent portions of the plate, when taken on glass, or by the natural dark colour of the ferrotype plate.

Two main points are to be attended to in the production of these Photographs.

First, to obtain an image distinct in every part, *but of comparatively small intensity.*—If the deposit of reduced metal be too thick, the dark background is not seen to a sufficient extent, and the picture in consequence is deficient in shadow.

Secondly, to *whiten* the surface of the reduced metal as much as possible, in order to produce a sufficient contrast of light and shade. Iodide of Silver developed

in the usual way presents a dull yellow appearance which is sombre and unpleasing.

The Collodion for Positives.—Ordinary Collodion iodized for Negatives and giving a thick yellow film, usually fails in taking good Positives. If the exposure in the Camera be sufficiently long to impress dark shadows, the lighter parts of the image develop with such rapidity that the gradation of tone is lost by excessive deposit of Silver. The addition of Nitric Acid to the Bath is to a certain extent a remedy, inasmuch as it lessens the intensity of the reduction and gives the Silver a sparkling appearance; nevertheless Positives taken in this way are always unpleasing, and cannot be compared with a good Daguerreotype in softness and delicacy.

A better class of picture may often be obtained by diluting down a sample of Collodion with Ether and Alcohol until it gives a pale bluish film in the Bath. The proportion of Iodide of Silver being in that case small, the action of the high lights is less violent, and the shadows are allowed more time to impress themselves.

The employment of a very thin film for Positives is not invariably a successful process. The particles of the Iodide of Silver being closely in contact with the glass, unusual care is required in cleaning the plates in order to avoid stains; and as the amount of free Nitrate of Silver retained upon the surface of the film is small, circular patches of imperfect development, causing blue and green stains, are liable to occur, unless the reducing agent be scattered evenly and perfectly over the surface. Also if free Iodine or organic substances which have a retarding effect on the action of light be present to a considerable extent, the Collodion will not work well with a small proportion of Iodide: in such a case a creamy and dense layer of the sensitive Salt is required, to give a sufficient power of resistance.

In attempting to dilute down the Nitrate Bath at the same time with the Collodion, we gain in some respects

an advantage. Excess of development is obviated, and the picture shows well on the surface of the film. The employment of a very weak Nitrate Bath (twenty grains of Nitrate of Silver to the ounce of water) in the Positive process is not however advisable on the whole. It becomes necessary, on account of the small quantity of Silver present, to exclude all free Nitric Acid, and even to avoid the employment of a Collodion too highly tinted with Iodine. On the other hand, with a strong Nitrate Bath, and a tolerably dense film of Iodide of Silver, a better result is often secured by the use of Nitric Acid, as will presently be shown.

These and other like processes, in which films of Iodide only are employed, have now been almost superseded by others, founded on a peculiar property which *Bromide* possesses when added in moderate proportion to an ordinary iodized Collodion. It alters the molecular state of the Silver reduced during development, rendering it metallic: the image also is superficial, and sufficiently translucent to give a perfect gradation of tone. When Bromide is employed, in conjunction with Sulphate of Iron as a developer, the quality of the Pyroxyline is not of the same importance as in the case of pictures taken with a simply iodized Collodion.

To produce a very faint and superficial image, a *weak* Nitro-Sulphuric Acid must be used for the Pyroxyline, but the objection is that after a certain point of dilution with Water, a quality of Pyroxyline is obtained which becomes *opaque* on drying. This is comparatively immaterial when transparent varnish is applied to the image, but it spoils the appearance of the picture when mounted without varnish, as is sometimes preferred.

With regard to the quantity of Bromide which may be introduced, the operator should be guided by the aspect of the developed image. If, when exposed long enough to form the shadows, the high lights appear too dense, more Bromide must be added: whilst, on the

other hand, if the Positive is grey and feeble, *and this defect is not due to over-exposure*, the proportion of Bromide may be reduced. The American operators, who are very successful with Collodion Positives, employ more Bromide than is recommended in this Work, but their Pyroxyline may possibly be made in a different manner.

One effect produced by Bromide in Positive Collodion, is seen in keeping the lines of the picture sharp and clear during development. When the Bath is strongly acidified with Nitric Acid and a simply iodized Collodion is employed, the image is often *blurred* by an irregular deposit of Silver, giving an appearance like defective focussing. With Collodion containing mixed Iodide and Bromide in the proper proportions, this does not so frequently happen, the image remaining clear and free from stains.

Does Bromide increase or diminish the sensitiveness of the film to a weak light? This is a question which can only be answered by considering the chemical state of the Collodion, Bath, and developer. With a weak solution of Pyrogallic Acid as a developer, and a dilute Bath, Bromide seems to *diminish* the sensitiveness considerably, but this appearance is delusive, since the latent image is really present, and simply requires a stronger reducing agent and more Nitrate of Silver to bring it out. On increasing the strength of the Bath therefore and using Sulphate of Iron as a developer, the whole of the details will show themselves after a minimum of exposure in the Camera.

There are states of Collodion also in which the use of Bromide may *increase* the sensitiveness—viz., when decomposition has taken place. Every practical operator learns by experience that Positive Collodion containing Bromide does not lose sensitiveness after iodizing in the same rapid manner as Negative Collodion prepared without Bromide. Doubtless the difference in the developing solutions—Sulphate of Iron in the one case and Pyrogallic Acid in the

other—has something to do with this result; but a peculiar action of the Bromide in rendering the Collodion independent of organic changes due to keeping after iodizing must be allowed.

A comparatively newly-iodized Collodion is seldom in the best possible state for taking Positives; for if it be colourless or nearly so, the plates will show clouding after development. By keeping the Collodion for several weeks, a portion of the Iodine is liberated, which has a great effect in giving brilliancy to the picture, by preserving the shadows from the reducing action of the developer.

The Nitrate Bath.—An ordinary neutral thirty-grain solution of Nitrate of Silver, such as is used for Negatives, may be employed also for Positives, and especially so if the Collodion be purposely kept after iodizing until it assumes a yellow tint, and liberates enough iodine to prevent the clouding which might otherwise take place in the absence of acid. Negative Baths, however, which contain Acetate of Silver, or any kind of organic matter, or which have been made from Nitrate of Silver previously decomposed by strong fusion, are not well adapted for Positives, since these conditions promote solarization, a defect which shows itself in Positives by discoloured whites on the most exposed parts of the film.

When the Nitrate Bath is made purposely for direct Positives, it is always better to acidify it with Nitric Acid rather than with Acetic Acid, as used for Negatives. The Nitric Acid diminishes the density of the deposited image, renders it whiter and more metallic, and assists in preserving the clearness of the plate. The mistake has sometimes been made of using too much Acid in proportion to the strength of the Bath, which not only lessens the sensitiveness of the film, but also, as before shown, promotes a blurring of the image, and a fogging from irregular reduction. Even with a Collodion containing Bromide, there will be a tendency to staining and imperfect development, if

the amount of Nitric Acid be carried as far as is sometimes recommended, in the case of a Bath of thirty grains to the ounce.

Many successful operators use a Bath of forty grains to the ounce for Collodion Positives, in order to shorten the exposure in the Camera, and give brilliancy to the image. This solution will bear a far larger addition of Nitric Acid than the ordinary Bath of thirty grains; and, always supposing Bromide to be present in the Collodion, satisfactory pictures may be obtained with a quantity of Nitric Acid as large as two minims to the ounce. Neither is the sensitiveness very much impaired by the excess of Acid; thus showing how many conditions have to be taken into account in considering the formation and development of the Collodion picture. With a Bath very strongly acidified, it would be impossible to get any result if the proportion of Nitrate of Silver and Iodide of Silver in the Collodion film were both reduced to one-half. The Acid and Nitrate of Silver must, in fact, be balanced against each other, and when the Collodion film is lessened in opacity, the developer must be considerably strengthened, otherwise the latent image, although actually present, cannot be made to appear in the half-shadows.

Our experience is not favourable to the employment of a forty-grain Bath in the Positive glass process as far as beginners in the Art are concerned. We find that there are fewer failures when the Bath contains thirty grains of Nitrate of Silver to the ounce, and is only slightly acid. Stains of reduced Silver at the edges of the plate are not easily avoided in the case of a strong and acid Bath, and if the developer is too weak, there are metallic spangles on the shadows.

Developers for Collodion Positives.—In the case of a Collodion which does not contain Bromide, Pyrogallic Acid is occasionally employed as a developer. When mixed with Acetic Acid, as is usual for Negative pictures, it produces a surface which is dull and yellow,

but this may be obviated by substituting a small quantity of Nitric Acid for the Acetic (Pyrogallic Acid, 2 grains; Nitric Acid, 1 drop; Water, 1 ounce). The surface produced by Pyrogallic Acid with Nitric Acid is lustreless, but very white, if the solution be used of the proper strength. On attempting to increase the amount of Nitric Acid the deposit becomes metallic, and the half-tones of the picture are injured; since Pyrogallic Acid, although an active developer, does not allow of the addition of mineral acid to the same extent as the Salts of Iron: it requires also, when combined with Nitric Acid, a fair proportion of Nitrate of Silver on the film, or the development will be imperfect in parts of the plate, producing green and blue stains; if such stains occur, a few drops of a solution of Nitrate of Silver may be added to the developer before use.

Sulphate of Iron.—This salt is a more energetic reducing agent than the last, and is better fitted for employment with a Collodion containing a portion of Bromide, the action of Bromide being to retard the development. To produce by means of Sulphate of Iron a dead white tint with absence of metallic lustre, it may be used in conjunction with Acetic Acid.

The addition of *Nitric Acid* to Sulphate of Iron modifies the development, making it more slow and gradual, and producing a bright sparkling surface of reduced Silver. Too much of this acid however must not be used, or the action will be irregular. The Nitrate Bath also should be tolerably concentrated, in order to compensate for the retarding effect of Nitric Acid upon the development. The blue and transparent films of Iodide of Silver, are not well adapted for Positives to be developed in this way. Such films require the most vigorous developer possible; Acetic Acid should therefore be used instead of Nitric Acid.

Protonitrate of Iron.—This salt is remarkable as giving a surface of brilliant metallic lustre without any addition of free acid. Theoretically, its action may be considered as closely corresponding to that of Sul-

phate of Iron with Nitric Acid added. There are however slight differences between them, which are in favour of the protonitrate, as regards the colour of the image.

The *Nitrate* is, of all the Protosalts of Iron, by far the most feeble developer, and is seldom used alone in Photography. In the case of Bromo-iodized Collodion very little dependence must be placed upon the Protonitrate of Iron as far as reducing Metallic Silver is concerned, but it may be added to Solution of Sulphate of Iron when the peculiar metallic tone which it imparts, is desired. Beginners often fail in using this developer, from not allowing a sufficient excess of the Sulphate of Iron in its preparation, and from supposing that the Protonitrate is equally as strong a reducing agent as the Protosulphate, whereas it is at least twenty times weaker.

The Tone and Colour of Positives.—The same chemicals yield such different results in the hands of various operators, that some have spoken of manipulation and practice as more essential than theory. Doubtless the exact time of exposure in the Camera is important, because a short exposure always produces an image of a whiter colour and more transparent shadow than a long exposure. In the case of Negatives, the image, viewed by transmitted light, is often of a jet-black when under-exposed, but of a ruby-red when over-exposed. So in Positives, it is always brighter and more metallic when the action of the light is stopped at the proper time. There are other causes of variation in the colour of the Positive image, such as changes in the actinic intensity of the light; and the operator may expect to produce a better quality of picture when the light is strong.

The gradation of tone in Collodion Positives will also be affected by the mode in which the light falls upon the subject; for when it possesses great actinic power, there is always a tendency to an excessive reflection from the high lights; and if this be not counteracted by an arrangement of curtains, to be described in

another part of this Work, it will require the utmost attention to the state of the chemicals, to prevent excess of intensity, and loss of good shading.

The mode of developing the Positive image has an effect upon the gradation, independently of the exposure, or of peculiarities in the Collodion. The theory is as follows :—When the Nitrate of Silver is present upon the film in large quantity relatively to the Sulphate of Iron, the tendency is to give great contrast of image, and to produce a bold picture, which appears to stand out from the glass. The deposit of Silver in such a case falls more abundantly upon the high lights, and less so upon the shadows, so that the shading in the face and lighter parts is often lost. On the other hand, when the quantity of Nitrate of Silver is much reduced in relation to the Sulphate of Iron, the image develops more slowly, and is soft and full of half-tone: in extreme cases the high lights are not sufficiently opaque, and the features of the sitter, after backing up with the black varnish, are those of a Negro. This rule applies to every kind of developed picture, and the practical inference from it is, that when the Positive is too vigorous, and the details in the face are lost, *a large quantity* of developing solution should be scattered over the film so as to wash off a portion of the free Nitrate of Silver. Experimental trial will convince the operator how extremely minute is the proportion of Nitrate of Silver actually required for the formation of the image; but no exact directions can be given, since the quantity will vary with the density of the sensitive film, the brightness of the light, the amount of retarding acid, and the strength of the developer.

Fixing Agents for Positives.—Hyposulphite of Soda is not usually employed for fixing Collodion Positives, since it contains Sulphur, and is somewhat unstable; hence the image is liable to be superficially darkened to an appreciable extent. Cyanide of Potassium is free from this objection, and always produces a whiter picture than Hyposulphite. The strong solvent powers

of Cyanide of Potassium must be borne in mind, when using it as a fixing agent; for if the solution be too concentrated or allowed to remain a long time upon the plate, the middle tints first become whitened from conversion into Cyanide of Silver, and immediately afterwards begin to dissolve. Neither should the plate be exposed to a strong light whilst the Cyanide is upon it, as the action of light favours the conversion of the image into Cyanide of Silver. Sulphocyanides of Potassium and Ammonium will probably be found useful fixing agents for Positives, as they are far less likely than the Cyanide to endanger the delicate half-tones of the picture.

A Process for Whitening Positives by Corrosive Sublimate.—In place of brightening the Positive image by modifying the developer, it was proposed some time since by Mr. Archer to effect the same object by the use of the Chloride of Mercury, HgCl.

The image is first developed in the usual way, fixed, and washed. It is then treated with a solution of the Chloride (thirty grains dissolved in an ounce of hot water), the effect of which is to produce almost immediately an interesting series of changes in colour. The surface first *darkens considerably*, until it becomes of an ash-grey, approaching to black; shortly it begins to get lighter, and assumes a pure white tint, or a white slightly inclining to blue.

The *rationale* of this reaction appears to be, that the Chlorine of the mercurial salt divides itself between the Mercury and the Silver, producing a compound of Calomel and Chloride of Silver, which is not affected by light.

Positive Photographs whitened by Chloride of Mercury have usually more or less of a bluish tone, but this may be overcome by associating other chemicals with the Corrosive Sublimate. A more serious objection is the instability of the picture after whitening, since it has been stated that these images are liable to fade unless special precautions be taken.

SECTION II.

ON COLLODION NEGATIVES.

As in the case of a direct Positive we require an image which is *feeble* though distinct, so, on the other hand, for a Negative, it is necessary to obtain one of considerable intensity. In the Chapter immediately following the present, it will be shown that in using glass Negatives to produce Positive copies upon Chloride of Silver paper, a good result cannot be secured unless the Negative is sufficiently dark to obstruct light strongly.

There are various conditions affecting the formation and development of a Photographic Negative, which ought to be studied by one who aims at perfection in the Art. Some of these are—the quality of the light at the time of taking the picture, the focal length and aperture of the Lens, the state of the atmosphere, etc. To meet the different cases which may arise, the Collodion, the Nitrate Bath, and the developing solution may each or all be considerably modified.

With regard to the first of these conditions we may observe that the mode in which a Negative develops, and its colour when the process is completed, vary much with the actinic intensity of the light. Pictures taken by a short exposure in a strong light, develop easily under the Pyrogallic Acid. The first deposit of Silver is often of a red colour when held against the light, and this influences the subsequent precipitation, so that the Negative continues to darken until the whole of the Nitrate of Silver in the film has been decomposed. When examined after fixing, it shows a plum-colour or yellow bloom by reflected light, and is often brown by transmitted light. In dull wintry weather, on the contrary, and especially when the atmosphere is loaded with aqueous vapour, the Negative picture is slow in appearing under the action of the developer, and the image first formed is rather of a violet-blue than of a red

colour. In consequence of this, the subsequent deposit of Silver is likewise of a violet-blue, and a much longer time is expended in bringing the development up to the proper point. The particles of precipitated Silver are always larger when the reducing process is slow, and thus Negatives taken in a bad light often prove in printing to be less intense than they appear, whereas those taken in a bright light are usually more intense chemically than visually.

When the strength of the light falls very low indeed, as, for instance, in working in a room covered in with glass of a greenish tint, fatal to quick Photographic action, the darker parts of the picture fail to impress the film, and the Negative shows only patches of black and white; or, with a more sensitive Collodion, the whole picture appears, but is extremely feeble and indistinct, a deposit of Silver falling upon the shadows and giving a cloudy aspect. On the other hand, in a light of extreme brilliancy, reddening from solarization is to be apprehended, the actinic rays being reflected from the high lights of the subject in a greater proportion than from the shadows: this may happen especially with a sky free from fleecy clouds, which when present have a great effect in illuminating the shadows and diminishing excessive contrast. When solarization of Negatives occurs from great intensity of light, the image often starts out almost instantaneously on applying the Pyrogallic Acid, and after fixing by the Hyposulphite of Soda exhibits an intensely red appearance of the high lights, with a steel-blue colour of the same parts viewed by looking down upon them.

We notice in the second place the focal length and aperture of the Lens, as a condition influencing the quality of the developed Negative. If, for instance, two Cameras be pitched side by side, at the same view, one being a Stereoscopic instrument with a single Lens of 4½-inch focus, and the other fitted with a twenty-inch Lens, suitable for glasses of twelve inches diameter, the plates, even when properly exposed, will behave

differently under the action of the developer, the Stereoscopic picture showing by far the greater intensity, contrast of tint, and tendency to solarization. The relative power of the Lenses makes the difference, the short-focus Lens producing a brilliant image which impresses the sensitive film in less than a third of the time required by the other. A second experiment, equally instructive, may be made by surrounding a group of statuary with a dark drapery, so as to produce a strong contrast of light and shade. On copying such an object with the full aperture of a short-focus Lens, it will be found almost impossible, unless the composition of the Collodion be modified in a manner presently to be explained, to get the whole of the picture simultaneously. Either the whites will be well rendered, and the blacks wanting, or by a longer exposure the shadows will be well brought out, but the lights solarized. Now take the same Lens and cut down the effective aperture by a middle-sized diaphragm, allowing proportionally longer time in the Camera, when a perfect Negative will be produced. This rule, then, may be stated as follows:—A Camera image of great actinic intensity often produces a Collodion Negative with exaggerated contrast of light and shade, and conversely an image of low intensity tends to give a picture which is too uniform, and deficient in extreme tints. Availing himself of this knowledge, the skilful operator alters the size of his diaphragms according to the quality of picture desired, and remedies solarization by diminishing the supply of light.

The amateur, on commencing Photography, is often at a loss to understand apparent discrepancies in the formulæ employed by various operators, and in their general mode of working. In one instance a plate of twenty inches by seventeen is developed to the full intensity with a single application of the reducing agent; in another, a Negative of half that size is found to require repeated treatment with Pyrogallic Acid and Nitrate of Silver, and to occupy ten or fifteen minutes

in reaching the full opacity. Supposing the Lens and chemicals to be the same in each case, the difference may depend upon *the character of the subject.* When a distant landscape is photographed, a large number of rays of light are concentrated upon the film: but if an object like an old picture or a faded drawing be copied without any reduction in size, the light is very feeble. No careful timing of the exposure will cause two such Negatives to develop in the same way, because the long-continued action of a weak light in the Camera does not correspond to the shorter action of an intense light. The molecules of Iodide of Silver are differently affected in the two cases, and consequently they behave differently when treated with the mixture which constitutes the developer.

The Collodion for Negatives.—A perusal of the last Chapter will show that the properties of Negative Collodion vary much with the mode of preparing the Pyroxyline. Distinguishing terms however are always useful, and hence we propose to speak of Pyroxyline *with*, and Pyroxyline *without* organic reactions towards the Salt of Silver; the former being the variety which yields the intense Negative images.

Pyroxyline without organic reactions may be expected to give the greater sensitiveness of the two, and the better keeping qualities after iodizing. It is however difficult to use it in consequence of the increased liability to fogging and spots of all kinds. Also when the intensity and contrast of the image are too small, as frequently happens with such Collodion, they cannot easily be increased, whereas excessive intensity may readily be reduced. The Pyroxyline *with* organic reactions is therefore preferred by the majority of operators.

For the sake of greater simplicity, the Author has given only one formula for Negative Pyroxyline in Chapter XI. of this Work. This formula appears to answer well for normal Collodion, applicable to all purposes. Those however who wish to prepare a

Pyroxyline suitable for any one especial kind of work, will find the subject examined more fully in another part of this volume.

Independently of the Pyroxyline, Negative Collodion may be described as of two kinds, the simply iodized, and the *Bromo*-iodized Collodion. Each has its advantages and likewise its defects. The first gives the greater sensitiveness, and also the greater intensity, but it is more liable to spots and markings, and the purity of the chemicals is of greater importance than when Bromo-iodized Collodion is employed.

Let us examine the above points more minutely. It must be allowed that the addition of a Bromide to Negative Collodion impairs the sensitiveness. Much indeed depends upon the mode of developing, but even when the reducing agent is strong, and the Nitrate of Silver abundant, the Bromo-iodized Collodion is still inferior in that respect. If such a Collodion be found on trial to yield a picture in eight seconds, a pure, simply iodized Cadmium Collodion will probably give the same picture in five seconds. Hence in the dull winter months, many are necessitated to employ Iodides alone, who at more favourable times use combinations of Iodide and Bromide.

The excessive sensitiveness of simply iodized Collodion however is not seen in perfection, unless all the materials are pure, and hence some have stated that the addition of a small portion of a Bromide increases the sensitiveness. Experiments leading to such a conclusion were probably made with a Collodion which from organic decomposition of the Pyroxyline or other causes, had acquired the property of producing an intense Negative, and in this case the action of the Bromide, as already shown in previous pages, is peculiar. A Pyroxyline without strong organic reactions is proper for the most sensitive iodized Collodion, and the Ether must also be very pure. When this extreme purity of the Ether cannot be secured, Iodide of Cadmium should be used in place of Iodide of Potassium, to

preserve the fluid in a neutral and colourless condition. The manufacturer of Collodion who examines its properties shortly after its preparation finds little or no difference between the Iodide of Potassium and the Iodide of Cadmium. The purchaser however usually esteems the latter to be superior as regards sensitiveness, because the plain Collodion has often been kept for a time before he obtains it, and has acquired the property of displacing Iodine: hence with the Potassium iodizer the colour changes quickly to orange-yellow, and the action of the light is retarded. Iodide of Cadmium, in consequence of its stability, would have superseded the other Iodides, had it not been for its glutinizing action on Pyroxyline, a serious objection in covering large surfaces of glass.

The effect of Bromide in diminishing the *intensity* of the image has already been considered in the section on Positives. It is often used for the same purpose in Negative Collodion, because when the light is strong and the Lens powerful, the intensity and contrast may be in excess, and if so, either a black and white picture without middle tints, or a red picture defective from solarization will be obtained. The Bromide effectually remedies both these causes of failure; frequently indeed it originates an error in the opposite direction. On looking at a Negative taken with a Bromo-iodized Collodion, we see that the peculiar metallic effect given by the Bromide is most evident in the half-shadows of the picture, where the light acts feebly. Provided there be a sufficiency of light, enough intensity will be obtainable in presence of Bromide, but when the light is too much reduced, the image will be rendered weak and translucent thereby. A Negative must possess a certain amount of intensity, and also a proper colour, if it is to possess what the Photographer terms "good printing qualities." These qualities cannot be secured by merely pushing the development and piling up particles of metallic Silver: much will depend upon the colour of the image in its

early stage, which should be of a soft red, and should appear nearly homogeneous when magnified. The employment of Bromide should be suspended when the particles of Silver become large and crystalline, since this condition of image is too permeable to the chemical Light in the process of printing.

The use of Bromides in Negative Collodion must be regulated by the nature of the Pyroxyline, as well as by the brilliancy of the light. The more marked the organic reactions of the Pyroxyline, the greater the proportion of Bromide admissible. This rule is the same as that laid down for Collodion Positives, and the directions are to examine the Negative, and if the contrast between the high lights and the shadows is too marked, to increase the quantity of Bromide. There are varieties of Pyroxyline which will not bear any addition of Bromide, the contrast of the image being too small, even with simple Iodide.

Apart from all considerations of density of Negative depending either upon the light or the Pyroxyline, it must be admitted that the employment of Bromide in Negative Collodion is most desirable for other and distinct reasons. The latent image produced in the Camera appears to be of a more definite description upon a Bromo-iodized than upon a simply iodized Collodion. In the case of the latter, disturbances of all kinds are apt to arise during development; the deposit is defective in one part of the plate, and irregular in another, so that to secure a Negative free from all blemish is a rare occurrence. Much indeed depends upon the skill of the operator and the purity of his chemicals, but this does not lessen the value of the Bromide, which undoubtedly exercises a remarkable influence in preventing, not only over-action of light, but likewise transparent markings, vertical lines, and spots of all kinds. Iodide of Silver, when associated with Bromide, receives the molecular modification in the Camera somewhat tardily, but when once impressed, it retains the image with greater force, and is not equally liable

to the reception of false images from moisture or traces of organic matter upon the glass.

Although in anticipation of our subject, we may here remark in addition, that those minor decompositions and impurities in the Negative Nitrate Bath, which so frequently disturb the image in the case of a simply iodized Collodion, will not produce the same effect when the film contains Iodide and Bromide conjoined. To prove the truth of this assertion, the Writer on one occasion collected several impure Nitrate Baths, none of which would yield a perfect Negative with ordinary Collodion, and yet he succeeded in every case in taking a good impression with Bromo-iodized Collodion. Bromide therefore may be viewed as a useful adjunct when retarding impurities of various kinds are present, against which the unassisted Iodide would be unable to contend.

The foregoing remarks on the comparative advantages of Iodized and Bromo-iodized Collodions apply more particularly to their use with a Pyrogallic developer. Experience has proved that the former, except under the exceptional conditions mentioned, is better adapted for a Pyrogallic, and the latter for an Iron developer. In the practical instructions it has therefore been deemed advisable to give separately the formulæ and the mode of manipulation which have been found most applicable to each kind.

Changes in Negative Collodion after Iodizing.—All Collodion loses sensitiveness more or less after iodizing, and especially so when the Pyroxyline is unstable and liable to part with a portion of its Peroxide of Nitrogen; also when the Ether is impure and in an ozonized condition. Practically we esteem a Collodion iodized with Iodide of Cadmium as uniform in properties, since if the chemicals are of good quality it will retain its sensitiveness nearly unchanged for twelve months after iodizing. Next in stability to the Cadmium Collodion stands the Bromo-iodized Collodion, which remains unchanged for a far longer time than a simply iodized

Collodion, and will retain a fair share of sensitiveness for many weeks.

Negative Collodion produces as a rule a more intense image when kept for a time in the iodized state; and this is true not only of Collodion iodized with the alkaline Iodides, but also of that containing Iodide of Cadmium. Bromo-iodized Collodion also gains in intensity as it gradually decomposes, and the quality of the Negatives is usually better after a few weeks' keeping than at first; they have more of a red or black tone, and exhibit greater contrast.

When alkaline Iodides are used, both the simple and the Bromo-iodized Collodion become more limpid by keeping. This is an advantage in coating full-sized plates, and since the setting powers of the Collodion are lessened, it becomes far easier to cover a large surface before gelatinization ensues. Old iodized Collodion of this kind is likewise more porous and permeable by the developer than newly iodized, which affords another reason why it is especially suitable for large plates.

Clearness of the transparent part in Negatives, with increased sharpness of outline, are both effects of keeping Collodion after iodizing. These peculiarities, as well as the comparative absence of spots and markings, are due partly to the "organic reactions" developed in old Collodion, and partly to the acid state of the film, when the Collodion is brown from free Iodine.

On keeping simply iodized Negative Collodion for a much longer time, the amount of free Iodine often becomes so great that the colour deepens to a red, and a portion of Nitric Acid is liberated on dipping the film into the Bath, sufficiently large to lower the density of the Negative, and make it grey and metallic.

The Negative Nitrate Bath, for Iodized Collodion.—In a previous Chapter the Chemistry of the Nitrate Bath was explained, with the action of organic substances upon it, and the marked effect which they produce upon the development of the Negative image.

Supposing the Nitrate of Silver to be chemically

pure, a question arises as to the proper state of the Negative Bath as regards strength, acidity, presence of Acetate of Silver, &c. On these points opinions are divided. Much depends upon the quality of the Collodion, and therefore the observations now to be made may be said to apply principally to the use of a simply iodized Collodion prepared by the formulæ given in this Work, and not to a Collodion containing both Bromide and Iodide.

Negative Baths have been used with as much as forty grains of Nitrate of Silver to the ounce of water; thirty grains, however, is quite sufficient, and any proportion beyond this would only add to the rapidity of development and tendency to staining in hot weather. When a Bath, originally made with thirty grains of Nitrate of Silver to the ounce of water, has been much used, the proportion of Nitrate will be found on analysis to have been considerably reduced. Ordinary Collodion dipped in such a Bath produces a less creamy film than usual, and the sensitiveness will be found to be much diminished.

The reaction of the Bath to test-paper ought to be either neutral or slightly acid, an alkaline reaction being always injurious. A neutral Bath produces a more dense Negative in dull weather, but is apt to give solarization in bright sunshine. The presence of Acetic Acid obviates this in great measure. An impression is not uncommonly entertained that any Acid in the Bath greatly diminishes the sensitiveness. With the Collodion described subsequently, the Writer does not find such to be the case, and therefore, in hot weather, and with a neutral colourless Collodion, he recommends that Acetic Acid should be used in the Bath to prevent rapid discoloration on applying the developer. A minim of the Glacial Acid may be dropped into each four or five ounces, if the subject be well lighted. In using an Acid Bath, however, the developer should be proportionally strengthened if the temperature or the light afterwards fall.

The use of *Nitric Acid* in the Negative Bath has been usually condemned as interfering with the precipitation of the Silver in the *opaque* form, but in this instance also everything depends upon the Collodion and the light. Pyroxyline with organic reactions tends so strongly to produce a brown or red image in bright sunshine, that the Collodion can be worked successfully in a Bath containing a trace of Nitric Acid. In circumstances favourable to rapid development and solarization, such as Stereoscopic Photography with Lenses of a short focus, the presence of a minute quantity of Nitric Acid is often a positive advantage, and no marked effect in preventing the development of details in the shadows will be perceived.

The employment of *Acetate of Silver* in the Bath met with much favour in the early days of Photography, but principally so because the preparation of pure Nitrate of Silver and the chemistry of Collodion were not understood. There is in fact an impurity common in commercial Nitrate of Silver which lowers the density of Negatives, and since Acetate always increases the density, its use has been found in such cases to be an improvement. So, again, Pyroxyline made at low temperatures and in weak acids produces a violet image, and hence Acetate of Silver, which changes the colour from blue to red, increases the intensity. When we add to this the fact that the presence of Acetate frees the Bath effectually from Nitric Acid, and thus enables a Collodion to be used which has been kept a long time, and is very brown from excess of free Iodine, it is not difficult to understand why it has been so extensively employed. If pure recrystallized Nitrate of Silver be selected in the first instance, and proper attention paid to the state of the Collodion, both as regards the length of time it has been kept after iodizing, and the quality of the Pyroxyline, full intensity of Negative may be obtained without the use of Acetate, even under somewhat unfavourable conditions.

The objections to the employment of Acetate of

Silver in the Bath are that it renders the solution more liable to change by keeping, favours red solarization in sunny weather, and at high temperatures increases the chance of spots, markings, and discoloration of the developer on touching the film.

The Negative Nitrate Bath for Bromo-iodized Collodion.—Experience has shown that a Nitrate Bath specially prepared for an Iodized Collodion with Pyrogallic developer, is not the best suited for a Bromo-iodized Collodion with Iron developer, and *vice versâ*. In the former case the aim is to obtain conditions of the Nitrate Bath which will combine the greatest sensitiveness with sufficient intensity of Negative at one development. When the chemicals are pure such a combination is easily attainable. In the latter case density and sensitiveness combined seem incompatible. But as intensity of image is quite under control, by a subsequent re-development, it is considered more important to prepare the Nitrate Bath almost entirely with the view of securing the highest sensitiveness. Acetate of Silver and Acetic Acid, which in the Nitrate Bath for Iodized Collodion often exercise a beneficial effect in increasing both density and sensitiveness, here act differently. They increase the intensity of image, but tend to lengthen the exposure. A small proportion of Nitric Acid, on the other hand, materially increases the sensitiveness, and at the same time lowers the vigour of the image; but since the latter can be raised to any extent by subsequent development, it is generally sacrificed in the first instance in order to secure the former. Directions for the preparation of this Bath will be found in another page.

Developing Solutions for Collodion Negatives.—Three formulæ are given subsequently, each of which has its advantages. The first contains Pyrogallic Acid with Acetic Acid; the second, Pyrogallic Acid with Citric Acid; and the third, Sulphate of Iron with Acetic Acid.

Developers for Iodized Collodion.—Pyrogallic Acid with Acetic Acid is the form most commonly employed

the use of the Acetic Acid being to moderate the violence of the action, and to preserve those parts of the Iodide which have not been touched by light. It has also the advantage of causing the solution to flow easily upon the film, thus forming a substitute for Alcohol, which would otherwise be required to prevent greasiness and streaks. The ordinary strength of the solution of Pyrogallic Acid is one grain to the ounce of Water, but as regards the quantity of Acetic Acid, the practice of operators varies. The intensity is greatest when the minimum proportion of about five minims to the ounce is used, but in this case a portion of spirit will be required in covering large plates. With a Negative Collodion giving abundance of intensity, it is better in every respect to employ the full strength of acid—viz., from twenty to thirty minims to the ounce, by which the reduction will be rendered more even, and stains of irregular action prevented.

Attention should here be drawn to the decomposition which commercial Pyrogallic Acid experiences by keeping. In the course of a very few days in hot weather the solution becomes yellow, and not only loses, in some measure, its power of developing the weakest radiations, but rapidly discolours the Nitrate upon the film. Solution of Sulphate of Iron also becomes yellow by keeping, but in this case no injurious effect results except in the weakening of the developer.

Pyrogallic Acid with *Citric Acid* may be viewed as a weaker reducing agent than the last, and one less likely to develop the dark shadows after a short exposure. Citric Acid, in fact, is an agent of far greater power in retarding reduction of Silver than Acetic Acid, and three-quarters of a grain will be found more than equivalent to twenty minims of the latter. This property of Citric Acid is an advantage when working at high temperatures, as, for instance, in a tent heated by the direct rays of the sun. The ordinary developer then acts so quickly that it is impossible to cover the plate before the reduction begins, and the discoloration on

touching the film is rapid, so that the pictures are almost invariably weak and red, with stains and spots. In this state of things a stronger Acid will be found serviceable, and although the ordinary proportions are twice as much of Pyrogallic Acid as of Citric Acid, yet in extreme cases the relative amount of Acid may be doubled, and a grain of each constituent of the formula be dissolved in an ounce of Water. The solution will flow evenly over the film on adding Alcohol, and the image will not appear until after an interval of twenty or thirty seconds. At so high a temperature the reducing power of even a feeble developer will be quite enough to bring out the shadows.

Citric Acid in the developing solution changes the colour of the Negative from brown to blue, and in consequence the real intensity of the image is somewhat less than it appears. It also has a marked effect in preventing red solarization in a brilliant light, and in preserving the surface of the film from fogging. Hence it is particularly adapted for distant landscape views including sky and water, or for other subjects well lighted; whilst, on the other hand, it is not suited for working in a glass house in a bad light and in cold weather, nor for copying works of art with long-focus Lenses, nor for taking interiors. In all such cases we may anticipate, when using a developer containing Citric Acid, that the image in its early stage of development will be weak and metallic, showing nothing of that tone of red which is so essential to the proper continuance of the precipitation. There will also be a loss of half-tint, from the reducing agent being too weak to bring out the darker portions of the image.

Pyrogallic Acid with Citric Acid forms a good developer for Cadmium landscape Collodion. Free Iodine being absent from this Collodion, the film on leaving the Bath is nearly neutral, and no Nitric Acid is present. Consequently the high lights over-act, and render the image very feeble unless the developer contain a stronger acid than Acetic Acid.

Sulphate of Iron is a developer of great power, and may be employed with advantage when its action is correctly understood. Being a substance belonging to the mineral kingdom, it is not favourably constituted for producing that *opacity* of image which is characteristic of Pyrogallic Acid; but on the other hand it is a much stronger reducing agent, and will bring out a perfect picture, when from some opposing conditions the ordinary developer proves ineffectual.

In order that an Iodized Collodion may be adapted for developing with Sulphate of Iron, so as to give sufficient intensity at one operation, it ought to be of that kind which gives strong contrast of image. It must likewise be a Collodion working clean and free from fogging, inasmuch as the Sulphate of Iron has a tendency to precipitate the Silver in an irregular manner upon the film greater than that of the Pyrogallic Acid.

The state of the Nitrate Bath must also be considered in making choice of a developer. Newly-prepared Baths which yield rather faint Negatives with Pyrogallic Acid, seldom succeed with Sulphate of Iron: the image becomes rapidly fogged and is useless. Baths made from fused Nitrate of Silver; Baths containing Acetate; and old Baths contaminated with organic matter, can on the other hand be worked more successfully with Sulphate of Iron than with Pyrogallic Acid. The rule appears to be that if the solution is in a state for giving very red Negatives with great intensity and freedom from fogging, the inorganic developer will be the better of the two: for in that case the organic reactions of the film are already at their maximum, and do not further need an organic developer like Pyrogallic Acid.

Depression of temperature is always an indication for the use of Sulphate of Iron, and in such a case its superiority is especially evident. When the thermometer sinks to 40° Fahrenheit, it will be found that the ordinary solution of Pyrogallic Acid and Acetic Acid

acts very slowly, and, in the case of Collodion which has undergone a little organic decomposition, it does not bring out the dark shades effectually, so that on examining the Negative after fixing, it appears to have received an insufficient amount of exposure in the Camera. An increase in the strength of the solution, using more of the Pyrogallic Acid and less Acetic Acid, does not altogether remedy the defect, although it adds to the opacity of the parts which have received most light. The substitution of Citric Acid for the Acetic would weaken the reducing power, and be a positive evil. Nothing then remains but either to warm the Bath and developing room by a stove, or to employ the Sulphate of Iron.

The difficulty of securing a proper gradation of tone is especially felt, not only in cold weather, but also when the picture embraces a variety of objects which contrast strongly in their power of reflecting light. Pyrogallic Acid as a developer is apt either to destroy the definition in the light parts by producing absolute opacity of the Negative, or to exhibit all the effects of over-action of light and red solarization. In this way the folds of white drapery suffer, and the distance in landscapes is lost. Such subjects can be photographed successfully, either by using a feeble Negative Collodion destitute of organic reactions, or by developing with Sulphate of Iron. Monuments of white marble standing out against the sky, with cypress-trees in the back-ground, have been well copied by using Sulphate of Iron; and although equally good results may be obtained with Pyrogallic Acid, by giving a long exposure and working with a small aperture to the Lens, yet this can only be expected when the Bath and Collodion are in the most perfect working order.

There are other causes of imperfect gradation of tone which Sulphate of Iron is employed to remedy. When, for instance, the atmosphere is yellow or murky, and no clouds exist to throw back the light into the shadows, it becomes very difficult to work a simply

iodized Collodion successfully with Pyrogallic Acid: the blacks of the Negative are too opaque, and the shadows too transparent. A longer exposure in the Camera in this instance is only a partial remedy, because it invariably *flattens* the picture, destroying its rotundity and stereoscopic effect. The use of Sulphate of Iron is exactly adapted to meet the case, for it has great power in developing weak radiations, whilst at the same time it precipitates the Silver in a comparatively metallic and translucent form. The resulting Negative is therefore soft, and free from violent contrasts of light and shade.

It has been said that the employment of Sulphate of Iron *invariably* shortens the necessary exposure in the Camera, but this statement is incorrect. That it does so in a bad light and at a low temperature is certain, but probably if the experiment be made under opposite conditions, the same result will not be obtained. In the case of a sun-lit view, for instance, taken in the spring months, the Writer finds Pyrogallic Acid abundantly strong enough to bring out the weaker radiations with a minimum of exposure, the Collodion being supposed to contain only Iodides.

Acetate of Iron has been used in Photography: it produces nearly as much density as Pyrogallic Acid, and at the same time is equal to the Sulphate in its power of developing the shadows. A similar effect may be obtained by mixing the ordinary Sulphate of Iron with half its weight of crystallized Acetate of Soda.

Effect of Varying the Mode of Development.—The remarks made in the last Section, on the contrast in Collodion Positives as affected by the mode of development, apply also in the case of Negatives. We have already seen that an ordinary Iodized Collodion may, when employed in the subdued light of a glass studio, produce a soft Negative, and yet in a glare of sunshine it may yield an intense Negative. If the intensity be greater than is desirable, it is in the power of the

operator to remedy it in a measure by removing a portion of the free Nitrate of Silver from the surface of the film. To effect this, it will only be necessary to flood the plate with a large quantity of a diluted solution of Pyrogallic Acid containing perhaps half a grain of the reducing agent to the ounce of water: or, more effectually still, to wash the plate with water, after exposure, and then to develop it by the addition of a few drops of the Bath solution to the Pyrogallic Acid. The picture thus obtained will have less contrast and solarization than before, and the developing action may be pushed far enough to bring out the deepest shadows, without adding too much to the intensity of the lights. When the converse of the foregoing happens, and the image on a simply Iodized Collodion is deficient in contrast, it is recommended to increase the relative proportion of Nitrate of Silver, by making an addition of that substance to the developer before applying it to the film.

Developer for Bromo-iodized Collodion.—However much opinions may be divided as to the relative merits of Pyrogallic Acid and Sulphate of Iron as developers for a simply Iodized Collodion, no doubt exists that the latter is the more suitable for a Bromo-iodized Collodion. The great reducing power of the Salts of Iron is precisely what we require in the presence of Bromide of Silver, a salt which considerably retards reduction; and, as already shown, the fine red or black tone which Pyrogallic Acid imparts to the Negatives is not seen when the Collodion contains Bromide. The tendency to produce fogging which the Salts of Iron exhibit in the case of a simply iodized Collodion, is nearly absent when the Collodion contains Bromide. A subsequent development with Pyrogallic Acid will almost in every instance be required, which renders the operation somewhat tedious, but it is amply compensated for by the increased vigour and contrast thereby obtained.

Fixing Agents for Negatives.—Cyanide of Potassium acts quickly in removing the Iodide of Silver, and the

plates do not require much subsequent washing; the film is also left in a favourable state for continuing the development with mixed Pyrogallic Acid and Nitrate of Silver when required. We recommended, however, Hyposulphite of Soda in preference to the Cyanide of Potassium, as safer in the hands of a beginner. Negative images are more easily dissolved by fixing agents than Collodion Positives, and therefore, unless much care be exercised, the application of Cyanide lowers the intensity materially, and whitens the surface of the picture by converting it into Cyanide of Silver. This is especially the case in working in the open air, and attempting to fix the image whilst the sun is shining upon the plate. Collodion Negatives developed with Sulphate of Iron are less soluble in solution of Cyanide of Potassium than those in which Pyrogallic Acid is used as the reducing agent; and the use of Bromide in the Collodion likewise diminishes the solubility.

Modes of Strengthening a Finished Impression which is too feeble to be used as a Negative.—The ordinary plan of pushing the development cannot be applied *with advantage* after the picture has been washed and dried. In that case, if it is found to be too feeble to print well, its intensity may be increased by one of the following methods:—

1. *Treatment of the Image with Sulphuretted Hydrogen or Sulphide of Ammonium.*—The object is to convert the metallic Silver into *Sulphide of Silver*, and if this could be done, it would be of service. The mere application of an Alkaline Sulphide has however but little effect upon the image, excepting to darken its surface and destroy the Positive appearance by reflected light: the structure of the metallic deposit is too dense to admit of the Sulphur reaching its interior.

This may be obviated by first converting the image into the white Salt of Mercury and Silver by the application of Corrosive Sublimate, and afterwards treating it with a solution of Sulphuretted Hydrogen or Sul-

phide of Ammonium. Negatives produced in this way are of a brown-yellow colour by transmitted light, and remarkably opaque to chemical rays. Instead of the Ammonium Salt, plain Ammonia diluted, Cyanide of Silver dissolved in Cyanide of Potassium, Solution of Hyposulphite of Soda, and other substances may be employed.

The employment of Corrosive Sublimate has one serious drawback—viz., the injurious effect which even a trace of a Salt of Mercury exerts upon the sensitiveness of Iodide of Silver: hence if the glass plates are not cleaned with extraordinary care, or if the slightest portion of the Mercury Salts finds its way into the Bath, injurious effects will follow. Some dispense entirely with the employment of the Sublimate, and act on the image with a solution of Iodine in Iodide of Potassium until it is converted into Iodide of Silver, after which the Sulphide is applied in the usual way. The Sulphide is in fact the principal agent in producing the intensity, and no other chemical is actually required, excepting for the purpose of rendering the image sufficiently porous to allow of a proper penetration by the Sulphur.

Another Process.—The image is converted into Iodide of Silver by treating it with a solution made by dissolving a grain of Iodine in an ounce of water by the aid of a little Alcohol. It is then washed,—to remove the excess of Iodine,—exposed to the light, and a portion of the ordinary developing solution, mixed with Nitrate of Silver, poured over it. The changes which ensue are precisely the same as those already described; the whole object of the process being to bring the metallic surface back again into the condition of Iodide of Silver modified by light, that the developing action may be commenced afresh, and more Silver deposited from the Nitrate in the usual way.

In a former edition a solution of Iodine in Iodide of Potassium was recommended for the conversion of the image into Iodide in this intensifying process. This

method, however, is liable to fail, for if the solution be kept upon the plate until the whole image becomes yellow, the sensitiveness to light is in great measure lost. At present therefore a weak aqueous solution of Iodine seems preferable, the condition of the film so produced being analogous to that of the Daguerreotype, the metallic Silver being acted on superficially, and never entirely converted into Iodide.

CHAPTER IX.

ON THE THEORY OF POSITIVE PRINTING.

THE subject of Collodion Negatives having been explained in the previous Chapter, we proceed to show how they may be made to yield an indefinite number of copies with the lights and shadows correct as in Nature.

Such copies are termed "Positives," or sometimes "Positive prints," to distinguish them from direct Positives upon Collodion.

There are two distinct modes of obtaining photographic prints:—first, by development, or, as it is termed *by the Negative process*, in which a layer of Iodide or Chloride of Silver is employed, and the invisible image developed by Gallic Acid; and second, by the direct action of light upon a surface of Chloride of Silver, no developer being used. These processes, involving chemical changes of great delicacy, require a careful explanation.

The action of light upon Chloride of Silver was described in Chapter III. It was shown that a gradual process of darkening took place, the compound being reduced to the condition of a coloured *subsalt;* also, that the perfection of the change was increased by the presence of excess of Nitrate of Silver, and of organic matters, such as Gelatine, Albumen, &c.

We have now to suppose that a sensitive paper has been prepared in this way, and that a Negative having been laid in contact with it, the combination has been exposed to the agency of light for a sufficient length of time. Upon removing the glass, a Positive representation of the object will be found below, of great

beauty and detail. Now if this image were in its nature fixed and permanent, or if there were means of making it so, without injury to the tint, the production of Paper Positive would be a simple department of the Photographic art; for it will be found that with almost any Negative, and with sensitive paper however prepared, the picture will look tolerably well on its first removal from the printing-frame. Immersion in the Bath of Hyposulphite of Soda however, which is essentially necessary in order to fix the picture, produces an unfavourable effect upon the tint, decomposing the violet-coloured Subchloride of Silver, and leaving behind a red substance which appears to be united to the fibre of the paper.

Other chemical operations are therefore required to remove the objectionable red colour of the print, and hence the consideration of the subject is naturally divided into two parts; first, the means by which the paper is rendered sensitive, and the image impressed upon it;—and secondly, the subsequent fixing and *toning*, as it may be termed, of the proof.

The present Chapter will also include, in an additional Section, a condensed account of the most important facts relating to the properties and the mode of preservation of photographic prints.

SECTION I.

Printing the Proof.

When a sheet of the photographically prepared paper is exposed to the light, we observe it to assume various colours, each one deeper and more intense than that which preceded it. These shades of colour are not always the same, but vary more or less with the mode of preparing the paper, as will presently be shown. The sequence of tints, in the case of a paper prepared simply with Chloride and Nitrate of Silver, is as follows:—Pale violet, violet-blue, slate-blue, bronze

or copper-colour. When the bronzed stage is reached, there is no further change.

On immersing the paper darkened as above described, in the fixing Bath of Hyposulphite, the violet tones are destroyed, and the print assumes a red or brown colour, which is most intense in the parts where the light has acted longest. Therefore we see, that, to produce a good photographic print, the Negative must possess considerable opacity in the dark parts; for if it be pale and feeble, the light passes rapidly through it and darkens the paper universally, before the exposure has been sufficiently prolonged to ensure the requisite degree of reduction; hence the deepest shadows of the resulting Positive are not dark enough, and there is a want of contrast which is fatal to the effect. A good Negative should be so opaque as to preserve the lights of the printed image beneath clear, *until the darkest shades are about to pass into the bronze or coppery condition*. If the amount of intensity be less than this, the finest effect cannot be obtained.

Let us now pass on to consider more carefully the exact function of each of the constituents of the sensitive sheet, and to show how the effect may be varied by altering their relative proportions, or by introducing substances not usually employed.

The printing process in its most simple form may be conducted as follows:—Take pure Swedish filtering-paper, free from size and other extraneous matters, and float it upon a solution of Nitrate of Silver containing about one hundred grains to the ounce of water: then dry and expose it to a strong sunlight. The darkening action will take place, but with such extreme slowness as at first to convey the impression that the paper is quite insensitive to light; by perseverance, however, for three or four days, a pale-brown tone will be obtained. One cause of this difficulty with the simply Nitrated paper is that the Nitric Acid in the Nitrate of Silver retards the reduction, and the pure fibre of

paper does not possess a sufficient affinity for Oxygen to enable it to overcome the opposition. It is possible however to counteract the Nitric Acid by adding Ammonia so as to produce Ammonio-Nitrate of Silver: this accelerates the change considerably, and a few hours' exposure to strong sunlight will then give the requisite opacity.

Swedish paper, however, although prepared with Ammonio-Nitrate of Silver, darkens very slowly, excepting in strong sunlight, and the Photographer will find by experiment that a minute quantity of Chloride of Silver in the prepared paper will enable him to obtain the desired result in *minutes* instead of *hours* of exposure. Other insoluble Salts of Silver, such as the Phosphate and Citrate, render the prepared paper more sensitive than when it has been treated with a soluble Salt of Silver only. The part therefore which we assign to such insoluble Salts is that of "accelerators" to the luminous agency, and of all accelerators the Chloride of Silver appears to be the most remarkable.

The following experiment will prove instructive in further exhibiting the function of the Chloride of Silver in ordinary sensitive paper. Take a piece of ordinary bibulous paper and float it for an instant upon the Nitrate of Silver solution which Photographers employ in printing; then blot it off, and immerse for five minutes in a solution of common salt containing ten grains to the ounce. This paper when freed from excess of salt by washing in distilled water, may be viewed as containing only Chloride of Silver in contact with the Cellulose. On exposing it to the light it will be found to change rather quickly to a pale-violet tone. At that point, however, the reducing action will be suspended, and when the fixing bath of Hyposulphite of Soda is brought to bear upon the image, it will nearly disappear in consequence of decomposition and solution. Pictures printed upon Chloride of Silver only would be altogether wanting in contrast, consisting only of half-tints, without any depth of shadow.

In a second experiment, take several strips of paper prepared as described for experiment No. 1, and apply washes of Nitrate of Silver of various degrees of concentration, such as 5, 10, 20, 40, 80, and 100 grains to the ounce of water. On drying the strips, and exposing them successively beneath the same Negative matrix, it will be found that the pictures become more and more vigorous in proportion as the Nitrate of Silver solution increases in strength, but that beyond a certain point a further increase in the concentration of the Nitrate of Silver does not add to the effect.

Having performed the above experiments, we are prepared to conclude therefrom,—that the office of the free Nitrate of Silver is to furnish the material which composes the metallic part of the image, and so to give *intensity;* the Chloride meanwhile accelerating the change and adding to the *sensitiveness* of the prepared paper.

It remains now to consider the action of the organic supporting basis, and this is perhaps equally important with that of the other constituents, although in the present state of our knowledge it cannot be defined with the same precision. If we take a sheet of Swedish filtering-paper and immerse it in cold Nitro-Sulphuric Acid, in such a way as to wet only one-half of the paper, the surface after washing and drying will consist in part of Cellulose and in part of Pyroxyline. Now it has already been shown that Pyroxyline is in a manner indifferent to the Salts of Silver, and that Chloride of Silver, supported by Pyroxyline, behaves in the sun's ray much in the same manner as Chloride of Silver supported upon a glass plate: hence we should anticipate that if a sheet of paper were converted only partially into Pyroxyline, and subsequently treated with Salt and Nitrate of Silver, the two halves would behave differently on exposure. This expectation is correct, and the experiment will show not only that the darkening is more decided upon the unaffected Cellulose, but that the image is less dissolved by the

fixing bath, and has a softer and more velvety shade of colour. In the one case the fixed print is of a warm red, and tones in solution of Chloride of Gold to a fine purple-black; in the other, it is very faint and metallic, or, if examined after toning, cold and slaty in aspect.

We may therefore add to what we have before said, the following statement, viz.—that whereas the function of the Chloride is to impart sensitiveness in Photographic printing, and that of the Nitrate of Silver to give intensity, the Organic Matter acts by brightening the *colour*. The artist requires an image which after simply fixing shall be of a *warm red tone*, and thus be capable of yielding a full brown or black on subsequent treatment with the Gold solution; he will find by experience that organic compounds of Silver in the paper, produced by adding Albumen or similar substances to the salting bath, will afford him the means of obtaining these varied tones, and that without them the picture will lack richness of effect.

The chemist may perhaps be disposed to inquire more particularly how the organic substance acts; but we must be guarded in answering this question, because it involves the consideration of a class of actions which belong to an obscure Chapter of Chemistry. It is known that many oxides and subsalts of metals, attach themselves in a peculiar way to animal and vegetable fibre, although the precise nature of the union is uncertain. These same Oxides commonly exhibit an affinity for the colouring matters used in dyeing, and are known as "Mordants," because they bind the colours on to the cloth and fix them so that they resist the action of water. An ordinary "iron mould" is a familiar instance of this kind of action, the red stain upon the linen consisting of an Oxide or Subsalt of Iron, adhering to the fibre. Organic substances saturated with Bichromate of Potash and exposed to light, furnish another example, for it has been shown that the Bichromate becomes in such a case reduced to an Oxide of Chromium, which is a true mordant, although

a feeble one. Now in the process of Photographic printing we suppose that besides the formation of Subchloride of Silver, Protoxide of Silver is reduced to the state of a lower or *sub*-oxide, and that this suboxide combines with the Cellulose. Further, the fact of the Cellulose or other organic matter having an affinity for a sub-oxide facilitates the formation of that substance, and enables it when formed to withstand the action of bodies like Hyposulphite of Soda, which are known to possess the property of decomposing Suboxide of Silver when existing in an uncombined state.

If Photographic printing can be shown to bear any analogy to the operations employed in the art of dyeing, it would be anticipated that certain kinds of fibre would exhibit the affinity for the mordant oxide more completely than others. It is well known, for instance, that woollen stuffs take certain dyes with more facility than materials made of linen or cotton, so that if a cloth be woven partly of wool and partly of cotton, a colour may be fast upon the former, but removable by washing from the latter. So in Photography we find that cotton immersed in Nitrate of Silver is less readily affected by the sun's rays than wool or silk. In speaking of the use of animal substances in printing, we must not indeed lose sight of the fact that these tissues invariably contain traces of Chloride and also of Phosphate. The pure animal fibre, however, is believed to play an important part in the process, quite independently of any inorganic salts. This action of the animal matters we now proceed to consider further.

Swedish paper, prepared with Chloride and Nitrate of Silver, although sufficiently sensitive, could not be used in Photography. The picture would exhibit a complete want of definition, and would also appear to be sunk in the substance of the paper so as to be seen more distinctly by transmitted than by reflected light. If the Salt were employed in anything like quantity, Chloride of Silver would form in loose flakes upon the surface, and would burst out and fall away into the

Bath. The *sizing* of Photographic paper has undoubtedly a mechanical action, keeping the chemicals upon the surface, and thus securing an even layer of Chloride of Silver in a state of excessive division. This however, as already shown, is not the sole use of the sizing, for when it consists of Albumen or Gelatine it communicates a fine red tint to the image, and gives what artists term an aspect of transparency to the whole picture.

If we examine the action of the animal sizing chemically, we find that Albumen, Casein, and Gelatine all withdraw from the Bath large quantities of Nitrate of Silver, so that the solution becomes continually weaker. A sheet of transparent Gelatine, allowed to well up by imbibing a solution of Nitrate of Silver of the strength of twenty grains to the ounce of Water, will appropriate nearly the whole of the dissolved Nitrate, so that the liquid expelled from it by squeezing will yield less than three grains of Silver to the ounce. The Gelatine forms with the Nitrate of Silver a compound which may be designated Gelatino-Nitrate of Silver, and which is highly photographic and colorific. Chloride of Silver thrown down in presence of this Gelatino-Nitrate, does not clot together in the same manner as the pure Chloride of Silver, but exists in a state of excessive division, and remains for a long time without subsiding to the bottom of the liquid. Exposed to light, the Gelatino-Nitrate of Silver darkens to a ruby-red colour; and Chloride of Silver precipitated from an aqueous solution of the Gelatino-Nitrate never assumes, in the sun's rays, the slate-blue colour characteristic of Subchloride of Silver, but changes quickly to a chocolate-brown tone. In the case of a paper sized with Albumen or Gelatine, and subsequently salted and rendered sensitive, the action of the light is evidently compound, for the Chloride decomposes at the same time that the Oxide of Silver is reduced by the animal matter. The behaviour of the darkened paper always varies with the proportion which the Chloride bears to the organic

substance: when the former is relatively large, the print exhibits the violet shades on its removal from the frame, and dissolves considerably in the fixing bath; but with the organic matters in excess, the colour of the print is brick-red from the very first, and the tones are less affected by the solvent action of the Hyposulphite of Soda.

FURTHER OBSERVATIONS ON THE PRINTING OF PHOTOGRAPHIC PROOFS.

In considering the process of Positive printing more carefully, we may divide it as follows:—The Paper; Salting Bath; Sensitizing Solution; Various Kinds of Organic Matter.

The Paper.—The quality of Paper sold for Photographic purposes is variable, and often inferior. A difference exists in the length and thickness of the fibre of various kinds of Cellulose, so that the resulting paper may be either coarse or smooth-grained. Its smoothness cannot be estimated until the print has passed through all the processes of fixing and washing, because by hot-pressing and other appliances it is easy to get up a fictitious glaze.

Supposing the paper to be properly made in the first instance, yet much will depend upon the perfection of the process adopted for sizing. The defects which occur in a paper badly sized are of the following kind:—First, portions of the finished pictures are pale in colour, and have a spotty appearance, due to an inequality in the imbibition of liquid by the paper; some parts of which being comparatively impermeable by the Nitrate of Silver, and others more porous, the surface is unequally sensitive, and darkens in an irregular manner. Secondly, when the sizing is very soft, the chemicals sink too deeply into the paper, and the proofs are what is termed *mealy*, and ineffective. Albumen, even when employed without any addition of water, gives very little glaze upon a paper of this kind, and no surface vigour can be obtained:

the sheets are often very tender, so that they become torn in the many washings to which the photographic proofs are necessarily subjected; and when Albumen is used, there is a strong tendency to a superficial *blistering* in the fixing bath, or in the washing waters, inasmuch as the Alkaline solutions used in toning tend to lessen the tenacity of the size. Thirdly, paper may be too strongly sized, and when such is the case the amount of gloss given by Albumen is considerable, but the prints are not easily toned in the Gold solutions, and are fixed with difficulty.

There are two principal modes of sizing paper: first, with a mixture of Starch and Resin partially saponified by an Alkali; and second, with Gelatine hardened by Alum. The first method is principally practised on the Continent, and the latter in the papers of home manufacture. Papers sized with Starch and saponified Resin have necessarily an *alkaline* reaction, whilst the Gelatine sized papers exhibit an acidity due to the Alum. In each case the paper improves more or less by keeping, because the size becomes gradually harder, and the sheets are, in consequence, less easily torn in the washings. Opinions are divided as to which mode of sizing is to be preferred, but the general impression is, that the Starch offers more mechanical advantages when Albumen is to be used in the salting solution, whereas the Gelatine size gives a better surface layer of Chloride of Silver in the case of plain salted paper prepared without Albumen. Towgood's paper is held in much esteem for printing by the Ammonio-Nitrate process, and probably answers better than any other in the market, but it is not well adapted for Albuminizing. Papier Rive, so called from the place where it is manufactured in France, is a starch-sized paper, with a hard, smooth surface, not easily permeable by liquids; hence it takes a high gloss on the Albumen. It is somewhat rotten in texture, and apt to tear in the washing, but it assumes a fine brilliant colour in the toning-bath, and is therefore much used for carte-de-visite and stereo-

scopic prints. The German paper, usually called Saxe, also starch-sized, is stronger in texture than the Rive, and well fitted for large photographs. From its more porous texture, it does not assume so high a gloss on the Albumen as the Rive.

The Photographic properties of the paper are much affected by the mode of sizing adopted, even when Albumen is afterwards used, for the picture is probably formed partly upon the Albumen and partly in the sizing. English papers tend to give red tones which become brown or chocolate-coloured in the finished print. This is due in part to the use of Gelatine, which, as before shown, forms a compound with Nitrate of Silver, darkening in the sun to a ruby-red colour; but in part to the Alum employed to harden the Gelatine, since Alum is an acid salt, and acids tend to impart a foxy-red tone to the image. The foreign papers, sized with Starch or Resin, produce tones which are of a sepia-brown after fixing, and of a purple-black when treated with the Solution of Gold; the reason is partly because the Starch and Resin do not, like Gelatine, exert a very marked action in reddening the picture, and partly because the sizing has an alkaline reaction, and alkalies are found to diminish redness, just as acids increase redness.

Many additional observations might be made on the colour of the image yielded by the various commercial qualities of Photographic paper, but the above general division into Gelatine-sized paper and Starch-sized paper will be sufficient. At the same time, it should be borne in mind that the manufacturer has it in his power, by adding small quantities of organic bodies to the size, to modify the tone given by the paper, even when employed in the albuminized state. Hence, although the general characters of a paper may be those of a Starch-sized paper, yet the print may assume a brick-red colour in place of a violet tone, in consequence of some addition made to the size.

Rendering the Paper Sensitive.—Under this head we

speak first of the salting solution, and second of the Nitrate Bath. Observe, in the first place, that the strength of both solutions should be properly adjusted, so that when the amount of Chloride of Silver in the paper increases, the excess of free Nitrate of Silver may increase also. Theoretically, three parts by weight of Nitrate of Silver will precipitate nearly one part by weight of Salt, and a slight excess of the Nitrate of Silver will remain. These proportions, however, are not always adhered to, because in Photographic printing there are many disturbing conditions. The sizing of the paper, and the Albumen glaze, appropriate a quantity of free Nitrate of Silver, as already shown; and not only so, but the proportions of Nitrate and of Chloride left in the paper vary with the method of applying the solutions. There are three modes of spreading solutions on photographic paper,—by brushing, by floating, and by total immersion. The first leaves a small, and the third a large amount of solid matter upon the paper, whilst the second gives a variable result according to the length of time the paper is left floating upon the Bath. Experience shows that for an Albuminized paper, both solutions being applied by floating, the Nitrate Bath should be about six times as strong as the Salting Bath, and should be left twice as long in contact with the paper. In the case of a paper *floated* upon the Salting Bath, and *brushed* with the Nitrate of Silver, the latter may be twelve times stronger than the former; and when the papers are salted by total immersion, and sensitized by brushing, the Salt may conveniently be reduced to a fifth of the ordinary weight, and the Nitrate of Silver left as before, so that the proportions may be nearly as thirty of Nitrate to one of Salt.

The strength of the Nitrate Bath in Photographic printing must also be regulated partly by the mode of sizing adopted. A hard-sized English paper keeps all the chemicals comparatively upon the surface, and does not require such concentrated solutions as a paper which

is more soft and spongy. Also, when any organic matter like Gelatine or Albumen is added to the salting bath, the amount of Salt must be lessened, because the glutinous character of such fluids causes more to be retained upon the surface of the paper. The difference in the atomic weights of the various soluble Chlorides used in salting must also be borne in mind; 100 grains of Chloride of Ammonium contain as much Chlorine as 109 grains of Chloride of Sodium, or as 228 grains of Chloride of Barium (see the Vocabulary).

The Salting Bath.—The foregoing remarks apply both to the Saline and to the Sensitizing bath; in those which follow, the two will be considered separately. The sensibility of Photographic paper is regulated up to a certain point by the amount of salt used in its preparation. The quantity of alkaline Chloride determines the amount of Chloride of Silver; and with a proper excess of Nitrate of Silver, papers are, up to a certain point, more sensitive in proportion as they contain more of the Chloride. Highly sensitized papers darken rapidly, and pass very completely into the bronze stage. Those containing less Chloride darken more slowly, and do not become bronzed with the same intensity of light. A Photographic print formed upon a paper highly salted and sensitized, is usually vigorous, with great contrast of light and shade; particularly so when the printing is conducted in a strong light. Hence it will be an advantage, with a feeble Negative, and in dull weather, to double the ordinary quantity of Salt; whereas in the case of an intense Negative, and with direct sunlight, the deep shadows will be too much bronzed unless the quantity of Chloride of Silver in the paper is kept low, so as to stop the action of the strong lights at a certain point, and thus to allow the feeble rays time to come forward.

With regard to the effect which the amount of Chloride in the paper exerts upon the colour and general appearance of the print, the following statements may be made:—Highly salted and sensitized

papers give a picture more nearly approaching to black, than those which, containing a small proportion of Chloride of Silver, are less sensitive to light. Hence in printing upon paper weakly sensitized, in order to bring out the finer details of a highly intense Negative, we find the image unusually red after fixing, and of a brown or mulberry colour when toned.

It is possible to carry the proportion of Salt too far in Photographic printing; in that case, even though the excess of Nitrate be properly maintained, the print appears cold and dull, because the Chloride of Silver is in too large quantity with reference to the organic matter. A reduction in the amount of Salt, on the other hand, simply leaves the image of less contrast, but does not destroy its velvety softness: transparency and warmth depending upon the organic matter, and not upon the Chloride.

The Nitrate Bath.—The compound on which a positive print is formed is a Chloride, or an organic Salt of Silver, with an excess of Nitrate of Silver; hence nothing is gained by increasing the proportion of Chloride of Sodium, unless at the same time an addition be made to the quantity of free Nitrate in the sensitizing bath.

Let us consider more minutely the appearances which present themselves when the Nitrate Bath is too weak. If a sample of the ordinary salted and albuminized paper be floated for two or three minutes upon a solution of Nitrate of Silver of the strength of twenty grains to the ounce of water, the quantity of Nitrate left upon the surface will be insufficient, and the following defects will appear:—The paper darkens on exposure, but it does not reach the bronzed stage, the action appearing to stop at a certain point. On placing the print in Hyposulphate of Soda, it becomes very pale, and, when tinted, looks cold and slaty, without depth of shadow. In almost all cases there exist on pictures of this kind large spots or patches of a paler colour than the surrounding parts, since the capillarity of the paper is unequal, and some portions absorb slowly.

The spots are most abundant at that edge of the paper which is uppermost in drying, and are nearly absent at the lower part where the excess of liquid drains down and becomes concentrated by evaporation. In a second experiment, the salted paper may be left as long as ten or fifteen minutes upon the same weak Bath : the result will be improved thereby, for the Albumen is allowed time to draw to itself more of the Nitrate of Silver. A third experiment may consist in dissolving forty grains of Nitrate of Silver in an ounce of water, and floating portions of the same paper upon it : the shadows will be deeper than before, and the colour warmer, but in all probability there will be room for further improvement, since a forty-grain Bath is scarcely strong enough for the foreign papers albuminized with a ten-grain Salt solution, although sufficiently so for the English albuminized paper of the same strength. Lastly, dissolve sixty grains, eighty grains, and a hundred grains of Nitrate of Silver in three separate ounces of water, and float upon each, when it will be found that the pictures are all good, and differ very little in appearance. If, however, the time of floating be reduced to a single minute, the Nitrate Bath of a hundred grains will prove the best; and some artists consider that, in Photographic printing, both time and money are saved by employing a highly-concentrated Nitrate Bath, and floating the papers upon it for not more than a minute. The defect which the Writer would apprehend under such circumstances would be a tendency to spottiness from uneven absorption by the paper, since a lengthened floating is certainly favourable to even precipitation of the Chloride.

Those precautions which are observed in making the Nitrate Bath for Collodion Negative Photography, are unnecessary in the case of the Bath for printing. We saturate the former Bath with Iodide of Silver, but the printing bath need not be saturated with Chloride of Silver, since this compound, although not absolutely insoluble in solution of the Nitrate, dissolves in a pro-

portion so small, that it may be disregarded. Neither is it actually necessary to examine the crystals of Nitrate of Silver for free Nitric Acid, for unless the sample of Nitrate be very impure, the retarding effect of the Nitric Acid will be inappreciable, and especially so in the case of albuminized paper, which possesses usually a slightly alkaline reaction.

A Nitrate Bath containing free Oxide of Silver, however, and giving an alkaline reaction to Litmus, would in some cases be injurious, since Alkaline Nitrate of Silver does not properly coagulate *Albumen*, and in consequence a Bath of this kind soon exhibits a white turbidity when the papers are floated upon it. There are certain qualities of albuminized paper sold in commerce, which tend to precipitate the same white substance in the sensitizing Bath, and the Writer believes this to be due in part to alkalinity. The *strength* of the Bath, however, must always be noted; for the weaker it becomes, the greater the tendency to dissolve away the albumen without coagulating it. In such a case the greater part of the Nitrate of Silver is converted into Chloride, and not being properly retained upon the surface of the paper by the coagulated Albumen, falls away into the solution.

Papers rendered sensitive upon a Nitrate Bath faintly acid with Nitric Acid, or with Acetic Acid, are less liable to spontaneous reduction in the dark: whereas papers prepared upon a Bath which has become alkaline from continued employment of an alkaline albuminized paper, or other causes, soon change on keeping.

Acetate of Silver exercises an important effect in the Photographic Negative Bath, but in the Bath for printing, its action is not very remarkable. The only perceivable difference is a little extra bronzing in the shadows, and an increased difficulty of keeping the paper without discoloration in the dark. *Organic matter* is also mentioned as greatly influencing the action of the Negative Nitrate Bath, but in the printing bath its effect is inappreciable, and even when the Bath

has become highly coloured by the Albumen, its action is nearly the same as at first. The brown coloration above alluded to is probably due to the gradual formation of a *Sub*-Albuminate of Silver, partially soluble in solution of Nitrate of Silver.

Before leaving this subject, we must advert for a moment to the employment of the compound known as Ammonio-Nitrate of Silver* in Photography. The advantage derived from its use is an increase of sensitiveness, and also of intensity in the image. Another advantage of the Ammonio-Nitrate is that the colour of the print is improved, the redness being diminished and a soft velvety aspect being given to the image such as would be difficult to secure, on plain paper, with simple Nitrate of Silver.

There are, however, disadvantages attending the use of Ammonio-Nitrate of Silver, which prevent it from being generally adopted. In the first place it does not coagulate Albumen, so that albuminized paper floated upon Ammonio-Nitrate of Silver loses its surface-varnish, and appears *dead*, like the plain paper. Secondly, it is more liable to spontaneous change, and to discoloration by traces of organic matter, than simple Nitrate of Silver; and hence when used as a Bath, it becomes perfectly black in the course of a few days, from sizing, etc., dissolved out of the salted paper. Thirdly, the action of the salted paper upon Ammonio-Nitrate of Silver liberates *free Ammonia*, as will be seen by referring to the Vocabulary, page 82, and this free Ammonia being a solvent of Chloride of Silver, attacks the sensitive coating and dissolves it, thus producing white lines and transparent markings. The latter objection is the most formidable of all, and in consequence of it the Ammonio-Nitrate has nearly fallen into disuse, excepting in the case of papers purposely prepared with a very small quantity of salt, so as to avoid the production of free Ammonia as far

* The Chemistry of Ammonio-Nitrate of Silver is explained in the Vocabulary.

as is possible. Such papers are economical, because a comparatively weak Silver solution suffices to sensitize them, and to give the requisite vigour to the shadows. The colour of the finished picture, however, on Ammonio-Nitrate paper feebly salted, is not black, but rather of a chocolate-brown, since the diminution in the quantity of Chloride increases redness, and the effect of the Ammonio-Nitrate of Silver in an opposite direction is not sufficient to counteract this tendency.

Organic Bodies used in Printing.—The most important of these is Albumen. Albumen is remarakble for producing a smooth and homogeneous layer upon the very surface of the paper, so that every detail of the Negative is rendered with an amount of distinctness which cannot be obtained in any other way. The prints are clear and brilliant, retaining even when dry much of the transparency which plain paper pictures exhibit only whilst in the water.

The main obstacle to the general adoption of Albumen is the difficulty of applying it evenly to the surface of the paper. Being a glutinous fluid, and not immediately amalgamating with the sizing, it is apt to run into lines when the paper is floated only for a short time, such as a few seconds; whilst on the other hand, if the paper be left for several minutes upon the Albumen, a portion of the size is dissolved, and the Albumen in consequence sinks into the paper, and does not impart the proper amount of gloss. In order to understand this, we must bear in mind that Albumen is not a neutral fluid, but possesses an alkaline reaction, due to the presence of a small quantity of Soda; hence, on adding Chloride of Ammonium to Albumen a development of free Ammonia takes place, easily perceptible to the smell, and Ammonia is a solvent of the materials used in sizing paper. To overcome this difficulty of applying the Albumen, and to obtain a greater amount of gloss, makers of albuminized paper have found it advantageous to expose the Albumen in an open vessel to the air, until a considerable amount of

evaporation has taken place. This evaporation does not always render the Albumen more glairy; on the other hand, the fluid often becomes gradually more limpid, acquiring a rather offensive odour, and an *acid* reaction to Litmus paper. Albumen so prepared runs upon the paper very easily, and does not dissolve the size, but it possesses some objectionable qualities, to be pointed out under the head of "Toning." That defects should arise from decomposition of Albumen, is not to be wondered at when we consider that one of the constituents of this substance is *Sulphur*, which during the putrefaction passes into the state of Sulphuretted Hydrogen, and is the cause of the offensive smell. The Nitrate Bath is soon rendered turbid by the use of stale albuminized paper, and the sensitiveness to light is injured, so that the half-tones of the picture do not appear until after a prolonged exposure. In preparing a highly albuminized paper, the requisite amount of evaporation may be effected over hot water at a temperature short of the coagulating point of Albumen; or what in most cases will be found sufficient, the wet Albuminized sheet may be rapidly dried by an ascending current of hot air. Pressing between heated rollers will still further condense the finished sheet, and give it the appearance of possessing a hard and glossy surface.

The reddening action of Gelatine, although greater than that of Starch, is less than that produced by Albumen, and the surface brilliancy is also less. Caseine, the animal principle of Milk, gives good definition, and a red colour like Albumen, but is destitute of gloss. Were it not for the difficulty of preparing soluble Caseine, it would probably come into more extended use, since the tone, when modified by a deposit of Gold, is very agreeable. Serum of Milk is a convenient form of employing a dilute solution of Caseine; since the rennet used in coagulating the milk does not separate the whole of the Caseine, but leaves a little dissolved in the liquid: by agitation with white of

eggs, and subsequently boiling, the suspended oil-globules may be entangled, and the Serum thus clarified.

Citrate and Tartrate dissolved in the Salting Bath exercise an effect upon the colour of the print quite as remarkable as that of Albumen. Paper prepared with Citrate, in addition to Chloride of Silver, darkens to a fine purple colour, which becomes brick-red in the fixing bath. Oxalate, however, has not the same action; paper prepared with Oxalate and Chloride of Silver darkening to a violet-blue colour, resembling that of the ordinary Subchloride. These facts will enable the reader to understand the remarks previously made on the composition of materials for sizing paper; and to see that the maker might, if so desired, introduce small quantities of organic substances capable of modifying the colour and general aspect of the print.

Amount of Silver in Sensitive Sheets.—To determine this point roughly, fifty whole sheets of Saxe paper, 18 + 22, albuminized with nearly pure Albumen, containing ten grains of Salt to the ounce, were floated for three or four minutes each, on a fifty-five grain Nitrate Bath measuring 137 ounces. The sheets were found to remove 17 ounces of liquid from the Bath, and to impoverish the remainder to the extent of five grains of Nitrate of Silver per ounce. The whole quantity of Nitrate of Silver absorbed by each sheet must, therefore, have been about half a drachm. In a second experiment, a quarter-sheet of albuminized Papier Saxe was dried and weighed; it was then floated for four minutes upon a forty-five grain solution of Nitrate of Silver, dried and weighed a second time: the gain in weight amounted to seven grains.

Preservation of Sensitive Sheets.—The discoloration of Sensitive Paper in the dark is due to a slow reducing action of organic matter upon the free Nitrate of Silver. The rapidity of the change varies much with the nature of the organic matter, but more so with the state of the Nitrate of Silver. Alkalies in the size of the papers or

in the sensitizing bath, facilitate the discoloration, whilst free acid and acid salts, like Alum, &c., retard it: hence French papers darken more quickly than English papers as a rule, and Ammonio-Nitrate paper is more unstable than that prepared with simple Nitrate of Silver.

The degree of dryness of the atmosphere in which the papers are kept also affects their rate of change, since moisture appears essential to the reduction. Hence the various contrivances devised for drying the paper, the best of which appears to be that of Mr. Spiller, in which a box is constructed with a false bottom pierced by holes, and lumps of quick-lime are placed beneath. To all such plans, however, there are some objections, for it has been found that papers, when rendered absolutely dry, do not darken vigorously in the light, and that it is necessary, in consequence, to leave them for a short time in close proximity to a damp cloth, until the requisite amount of water has been absorbed. Others, again, have observed that, although Sensitive Papers, kept for many months in a drying Box, may print to a sufficiently deep shade, yet that the image does not tone in the Alkaline Gold Bath so readily as a print upon newly-sensitized paper.

SECTION II.

Toning the Proof.

By the term "toning" we understand the removal of the reddish colour described in the first Section as the proper tint of a Photographic Positive, after the compounds of Silver unacted upon by light have been extracted by an appropriate fixing bath. Colours approaching to brick-red are in themselves so unartistic that from the very first discovery of Photography means were tried of removing them; and the employment of *Sulphur* was the plan originally adopted for that purpose.

TONING BY SULPHUR.

It is well known that articles of Silver plate become darkened by exposure to the fumes of Sulphur, or to those of Sulphuretted Hydrogen, of which minute traces are always present in the atmosphere. If the stopper of a bottle of Sulphuretted Hydrogen water be removed, and a simply fixed Photographic Positive suspended over it, the picture will lose its characteristic red tone and become nearly black. The black colour is even more intense than an experienced chemist would have anticipated, because analysis teaches us that the actual quantity of Silver present in a Photographic picture on paper is infinitesimally small, and it is well known that Sulphide of Silver, although of a deep brown colour, approaching to black, when in mass, exhibits a pale-yellow tint in thin layers, so that a mere film of Silver converted into Sulphide possesses very little depth of colour. To explain the difficulty, it has been suggested that the toning action of Sulphur on a red print is probably due to the production of a *Sub*-Sulphide possessing an intense colorific power, like the Sub-Oxide and Sub-Chloride of Silver. When the toned picture is subjected to the further action of Sulphur, it is converted into the ordinary Protosulphide of Silver, and becomes yellow and faded.

It is not necessary to enter into any details of the various processes originally recommended for toning prints by means of Sulphur. The principle was the same in all, but the mode in which the Sulphur was set free and brought to bear upon the proof varied. Commonly, a solution of Hyposulphite of Soda was mixed with some chemical which gradually decomposed it. Everything requiring explanation under this head will be treated in the next Section, when we speak of the properties of the Hyposulphite fixing Bath.

TONING BY GOLD.

After the Sulphur toning process had been discarded,

the Salts of Gold were used for improving the normal colour of the Paper Photograph, and the merit of first introducing them is due to M. Le Grey, of Paris. These methods, being still in vogue, will require a detailed description.

The Single Fixing and Toning Bath.—A simple mode, and one even now sometimes followed, is to add Chloride of Gold to the ordinary fixing bath of Hyposulphite of Soda. The prints are immersed in the resulting liquid immediately on taking them from the frame, and the first action of the "fixing and toning bath" is to dissolve out the unchanged Silver salts, and to leave the image of the usual red colour. Shortly however the red colour begins to pass gradually into blue or black, and the toning is complete.

At first sight the above process appeared correct both as regards theory and practice. A more extended experience however led to its condemnation, for it was found that the improvement of the colour was not due to a simple precipitation of Gold upon the surface of the image, as had been at first supposed, but partly to a deposit of Gold and partly to a communication of Sulphur. When a solution of Chloride of Gold is added to Hyposulphite of Soda, we have in the liquid not only the double Hyposulphite of Gold and Soda known by the name of Sel d'Or, but also a portion of the unstable Tetrathionate of Soda, prone to liberate Sulphur. The action of the Bath is therefore complex from the very first, but becomes more so on keeping the solution for a time, since spontaneous decomposition ensues, as will be more fully shown in the next Section. Practical Photographers were not slow in discovering that the fixing and toning Bath was inconstant in its action, and that although the prints were coloured with as much rapidity in an old as in a newly-mixed Bath, yet that the tints were more fugitive in the former case than in the latter. The reason was that whereas the newly-prepared Bath acted mostly by depositing Gold, and only partially by communication of Sulphur, the old Bath, on

the other hand, toned the prints entirely by Sulphuration. The reader will doubtless be surprised to hear that the colours produced upon the Photographic picture by means of Gold closely resemble those obtained by Sulphur; yet such is the case, for although shades of *blue* are characteristic of Gold, and shades of *brown* of Sulphur, yet it requires a practised eye to distinguish between them, and prints toned by Sulphur often possess the fine purple-black which many suppose to be due to a deposit of Gold.

In the Gold toning process, as now employed, all danger of Sulphuretting the prints is avoided. Hyposulphite of Soda having been proved to suffer decomposition in presence of Chloride of Gold, we no longer mix the two solutions, but prefer to tone the picture first, and fix it subsequently. The colouring action of a simple solution of Chloride of Gold upon the Photographic image may be thus explained:—The Chlorine previously in combination with Gold passes to the reduced Silver salt, bleaching the lighter shades by converting them into the white Protochloride of Silver, and imparting to the shadows a deep violet tint due to the production of Subchloride of Silver; at the same time metallic Gold is deposited, but its effect is not very clearly seen at this stage of the process, since a deep violet colour of nearly equal intensity may be obtained by using a solution of *Chlorine* in place of Chloride of Gold. If however the toned proof be acted upon by a fixing bath of Hyposulphite of Soda, all that portion of the violet colour which depends upon Subchloride of Silver will be destroyed, since the Subchloride is decomposed by fixing agents. Another portion of the colour will resist the action of the Hyposulphite, and this is probably Metallic Gold.

During the whole process of toning in solution of Chloride of Gold we observe a gradual lowering of intensity in the image; it has been found that this destructive effect is greater when the solution of the Chloride contains free Hydrochloric Acid, and that it

is lessened by the addition of an alkali: hence the employment of *alkaline* solutions of Chloride of Gold, first introduced in this country by Mr. Waterhouse, of Halifax, must be deemed an improvement.

The question as to the manner in which the alkali acts in preventing the image from being eaten away has been variously answered. The first effect of adding Carbonate of Soda to Chloride of Gold is to neutralize the free Hydrochloric Acid which that compound invariably contains, and thus to produce a double Chloride of Gold and Sodium. Now it has been suggested that this Chloride of Gold and Sodium is the real toning agent;—that the process consists essentially in the substitution of Gold for Silver, and that a double Chloride of Gold and Sodium becomes a double Chloride of *Silver* and Sodium, Metallic Gold being at the same time thrown down, and taking the place of the Silver of the proof. Further, it has been urged that in the alkaline toning process lies the real key to the production of permanent Photographic pictures, since the image of Silver, proved to be unstable, is by it converted into an image of Gold, not prone to change. These views are ingenious, but it is doubtful whether they express the truth; for on subjecting the image to the action of Chloride of Gold, we do not find that an atom of Silver is dissolved for each atom of Gold deposited, whilst as regards the entire conversion of the image into Metallic Gold, it may be shown to be impracticable. MM. Davanne and Girard have suggested that the alkaline addition to the Chloride of Gold is useful in neutralizing traces of free Nitric Acid, always liberated when the organic matter reduces the Nitrate of Silver in the process of printing. Undoubtedly the Positive on its removal from the printing-frame, has an acid reaction, and the Carbonate of Soda in the toning bath must operate beneficially in neutralizing it. This, however, is not the sole use of the alkali, according to the Writer's experience: it probably acts also by converting a portion of the Chloride of Gold into an Oxide of

Gold, which is an unstable substance, and may be made to yield up Metallic Gold to the proof.

When Carbonate of Soda is added to Chloride of Gold the change into Oxide is at first only partial, and an Oxychloride of Gold is probably formed. The Oxide of Gold, or Auric Acid, does not appear of itself to possess the power of toning the picture; and hence the *total conversion* of the Chloride under the influence of the alkali renders the Bath useless to the photographer. If, however, a portion of the Gold still remains in the form of Chloride, and the toning action can once be started, a spontaneous decomposition of the Oxide of Gold will take place by catalysis, and a larger quantity of Gold will thus be thrown down without the same injury to the print from communication of Chlorine. These views may appear complex, but they have been adopted by the Author after a careful study of the properties of the alkaline Aurates.

The alkaline substance usually employed for admixture with Chloride of Gold is the Carbonate of Soda, but it has been shown by Mr. Maxwell Lyte that an alkaline Phosphate or Borate produces the same effect. Others again have used an *Acetate*, and it will probably be found that any salt in which the alkaline constituent is combined with a weak acid will answer the purpose. In such cases the solution of the Chloride of Gold gradually becomes colourless by an interchange of elements, as above described.

CONDITIONS WHICH AFFECT THE ACTION OF THE ALKALINE GOLD TONING BATH.

a. *Degree of Concentration of the Bath.*—The exact amount of dilution with water in the alkaline toning bath is not of much consequence. A strong bath acts quickly, but is more liable to destroy the middle tints than a weaker solution left upon the image for a longer time. The proportion of Carbonate of Soda is also of minor importance, but it is desirable to use the mini-

mum quantity, since a highly alkaline liquid dissolves the size of the paper, and causes a blistering of the Albumen when the picture is laid in the fixing bath.

b. *The length of time after mixing.*—The two solutions of Chloride of Gold and Carbonate of Soda may be kept separately for any length of time, but on mixing them a chemical change ensues, and the liquid gradually loses its yellow colour. When the solution has become *nearly* colourless it is in the best state for use, and will remain so for many hours, but after a longer keeping of days or weeks it loses its activity, and deposits Gold in the metallic state on the sides of the bottle : alkaline solutions of Chloride of Gold being easily reduced by traces of organic matter.

c. *Presence of free Nitrate of Silver on the surface of the Proof.*—It is quite necessary to wash away the free Nitrate of Silver from the pictures before they are immersed in the toning bath, otherwise the Bath will become turbid and discoloured. Nitrate of Silver added to an alkaline solution of Chloride of Gold throws down not only Carbonate of Silver and Chloride of Silver, but also a brown powder, consisting of Peroxide of Gold, or Metallic Gold, and the supernatant liquid contains little else than Nitrate of Soda.

d. *Temperature of the Solution.*—The action of the Bath is much increased by carefully heating it to about 120° Fahr. before the prints are immersed, and this method has also the advantage of bringing the solution at once to the *nearly* colourless condition, in which it contains more Oxide and less Chloride of Gold. The plan of warming the Bath, however, is not often adopted by operators, since a similar result can generally be obtained by continuing the action of the cold solution for a longer time.

e. *Presence of Iodide of Silver.*—When Iodide of Silver is present in a proof, the toning action of the alkaline Chloride appears to be less rapid than when the image is formed on Chloride only. Hence sensitive paper is not improved, but rather the contrary, by

associating Iodide with the Chloride in salting, as some authors have advised. It is also unwise to employ a Nitrate Bath which has been previously used for Negatives, and contains Iodide of Silver dissolved. On floating the Paper upon such a Bath, the Albumen abstracts the Iodide from it in virtue of a chemical affinity, and the printed proof upon such paper remains for a comparatively long time in the toning solution without being coloured by the Gold.

f. *Mode of Preparing the Paper.*—The preparation of the paper is a matter of greater nicety in the alkaline Gold toning process than in the old mode of toning prints by Sulphur, since the affinity which secures the colouring action is stronger in the latter case than in the former. By adding an alkali to Chloride of Gold you improve the colour of the print, but retard the process of colouring, since, as before shown, the Oxide of Gold produced by the alkali is of itself nearly or quite inert, and the Chlorine is the element which possesses the affinity for Silver, and thus determines the change. Hence, although a defective sample of paper may tone evenly in a Sulphur Bath, in the case of the alkaline Gold Bath, there would be either spots or markings, which would remain of a red colour and refuse to tone.

One cause of unevenness of toning is an improper mode of applying the Albumen to the paper; for Albumen being a glairy substance, and having a strong tendency to run into lines, much will necessarily depend upon the manipulation. We might indeed remedy this defect by avoiding the use of Albumen, but it is found that in the Chloride of Gold toning process, the proofs acquire an inky shade, unless the image is printed upon the maximum quantity of organic matter, so as to encourage redness as much as possible. A hard-sized gelatinous English paper, with a minimum of Chloride in the salting bath, or a foreign starch-sized paper, salted with a mixed Citrate and Chloride, will produce an agreeable effect. Mr. Waterhouse, of

Halifax, gives a formula in which the organic matter is Caseine dissolved in highly dilute potash; there is no gloss, and the finished pictures are of a purple tone. If Albumen be used, the quality of the paper itself will be the principal point to attend to; but, in addition to this, the state of the Albumen must be noted, since sourness and decomposition are injurious not only to the sensitiveness of the paper, but also to the rapidity of toning.

Additional experiments on the conditions of the paper affecting the toning action are much needed. To further their prosecution the Writer ventures to give his experience, as follows:—the more metallic the image, the greater the rapidity of toning by Chloride of Gold, but the more inky the colour. Organic bodies which encourage the production of a subsalt of Silver under the influence of the light, hinder the deposition of Gold, but improve the colour by imparting a shade of red. There are however differences between these organic bodies, ascertainable only by experiment, for although Albumen and Citrate both favour the reduction of the Silver to the state of a subsalt, it will be found on trial that Citrate papers tone with greater facility than albuminized papers. Mr. Mabley, the Honorary Secretary of the Manchester Photographic Society, states that the image toned more rapidly when the paper was excited on a Silver Bath containing a little free Nitric Acid: this accords with theory, because, in presence of a strong acid, the reduction approaches more nearly to the state of metal—nevertheless the colour so obtained is not agreeable, and a warmer shade will usually be produced by albuminized paper which on its removal from the printing frame exhibits an image of a brick-red, and not of a violet-blue tone.

g. *Time of Keeping the Paper.*—If a print be formed upon albuminized paper, and kept for a long time before toning, there will commonly be some difficulty in securing a strong deposit of Gold. This is pro-

bably due to a change which takes place in the paper, from the organic matter reacting by degrees upon the Nitrate of Silver, and it has been stated that the same change is more gradually produced when the sensitive papers are preserved for many months in a dry state by means of Chloride of Calcium or Sulphuric Acid; such papers darken in the sun, but if the print be subjected to the action of a Gold toning bath at the same time with one on paper newly sensitized, the latter will be found to tone with the greater rapidity.

SECTION III.

Fixing the Proof.

The conditions for a proper fixing of the proof are not always understood by operators, and consequently they have no certain guide as to how long the prints should remain in the fixing Bath.

The time occupied in fixing will of course vary with the strength of the solution employed: but there are simple rules which may be followed. In the act of dissolving the unaltered Chloride of Silver in the proof, the fixing solution of Hyposulphite of Soda converts it into Hyposulphite of Silver (p. 147), which is soluble in an *excess* of Hyposulphite of Soda. But if there be an insufficient excess,—that is, if the Bath be too weak, or the print removed from it too speedily,—then the Hyposulphite of Silver is not perfectly dissolved, and begins by degrees to *decompose*, producing a brown deposit in the tissue of the paper. This deposit, called measles, which has the appearance of yellow spots and patches, is not usually seen upon the surface of the print, but becomes very evident when the print is held up to the light, or if it be split in half, which can readily be done by glueing it between two flat surfaces of deal, and then forcing them asunder.

The Reaction of Hyposulphite of Soda with Nitrate of

Silver.—In order to understand more fully how *decomposition* of Hyposulphite of Silver may disturb the process of fixing, the peculiar properties of this salt should be studied. With this view Nitrate of Silver and Hyposulphite of Soda may be mixed in equivalent proportions—viz., about twenty-one grains of the former salt to sixteen grains of the latter, first dissolving each in separate vessels in half an ounce of distilled water. These solutions are to be added to each other and well agitated; immediately a dense deposit forms, which is Hyposulphite of Silver.

At this point a curious series of changes commences. The precipitate, at first white and curdy, soon alters in colour; it becomes canary-yellow, then of a rich orange-yellow, afterwards liver-colour, and finally black. The *rationale* of these changes is explained to a certain extent by studying the composition of the Hyposulphite of Silver.

The formula for this substance is as follows:—

$$AgO,S_2O_2.$$

But AgO,S_2O_2 plainly equals AgS, or Sulphide of Silver, and SO_3, or Sulphuric Acid. The acid reaction assumed by the supernatant liquid is due therefore to Sulphuric Acid, and the black substance formed is Sulphide of Silver. The yellow and orange-yellow compounds are earlier stages of the decomposition, but their exact nature is uncertain.

The instability of Hyposulphite of Silver is principally seen when it is in an isolated state: the presence of an excess of Hyposulphite of Soda renders it more permanent by forming a double salt, as already described at p. 147.

These facts explain the reason why, in fixing Photographic prints, a brown deposit of Sulphide of Silver sometimes forms in the Bath and upon the picture. To obviate it, observe the following directions. It is especially in the reaction between *Nitrate of Silver* and Hyposulphite of Soda that the blackening is seen, the

Chloride and other insoluble Salts of Silver being dissolved, even to saturation, without any decomposition of the Hyposulphite formed. Hence, if the print be carefully washed in water to remove the soluble Nitrate, a comparatively weak fixing bath may be employed. But if the proofs are taken at once from the printing frame and immersed in a dilute Bath of Hyposulphite (one part of the salt to six or eight of water) without any previous washing, *a shade of brown* will be observed to pass over the surface of the print, and a large deposit of Sulphide of Silver will form as the result of the decomposition. On the other hand, with a strong Hyposulphite Bath there will be little or no discoloration, and the black deposit will be absent even when the prints are immersed with the free Nitrate of Silver still upon the surface.

The print must also be left for a sufficient time in the fixing bath, or some appearance of brown patches, visible only on looking through the paper, may occur. Each atom of Nitrate of Silver requires *three* atoms of Hyposulphite of Soda to form the sweet and soluble double salt, and hence, if the action be not continued sufficiently long, another compound will be formed almost insoluble, and with a greater tendency to decompose into Sulphide of Silver. Even immersion in a new Bath of Hyposulphite of Soda will not fix the print when once decomposition of Hyposulphite of Silver has commenced. The yellow or brown compound is not entirely soluble in Hyposulphite of Soda, and consequently remains in the paper.

Another important matter to observe in fixing Photographic prints is the *temperature* of the fixing bath. When Hyposulphite of Soda is first dissolved in water, much heat is rendered latent, and the solution in consequence is almost at the freezing point. In this state of things prints are fixed slowly and with difficulty, whereas at 70° or 80° Fahr. the action is more rapid. In the cold winter months Positives should be left in the Bath at least twice as long as in the summer months,

to prevent the occurrence of brown patches of imperfect fixation in the substance of the Paper.

The nature of the sensitive surface to be cleared of its superfluous Silver salt must also be considered in estimating the strength of Bath and the time of immersion likely to be required. Albuminized paper, from the horny nature of its surface coating, requires a longer treatment with the Hyposulphite of Soda than plain paper requires; and not only so, but it must be borne in mind that the Albumen has a property of combining with Nitrate of Silver and forming an insoluble salt which is more difficult of solution than Chloride of Silver. Gelatine also combines with Nitrate of Silver, and therefore the mere washing of a gelatinized sensitive paper for a few minutes in cold water does not remove the whole of the free Nitrate. It is better in all such cases to make the fixing bath far stronger than theory would indicate as sufficient for the solution of simple Chloride of Silver, otherwise it will be found that the fixing will be insufficient, and that there will be mealy spots in the print; although on adding recently precipitated Chloride of Silver to the Bath of Hyposulphite it immediately dissolves.

The Writer has noticed that when sensitive paper is *kept for some time* before being used for printing, yellow patches of imperfect fixation are very liable to occur. The Nitrate of Silver appears gradually to undergo a partial reduction by the organic matter, and cannot then be so easily extracted by the fixing bath. It has also been observed that albuminized and salted paper, when kept in a damp place, or exported to warm and damp climates, is liable to undergo a decomposition, in consequence of which the fixing bath fails to extract the whole of the superfluous Silver after printing, and the whites remain discoloured and spotty.

It has been recommended by some writers on Photographic chemistry to saturate the fixing bath with common Salt, in order to convert any Nitrate of Silver left in the proof by imperfect washing, into Chloride, and

thus to prevent blackening from decomposition of Hyposulphite of Silver. An excess of salt undoubtedly has the effect thus ascribed to it, but it appears to the Writer that its use is contra-indicated by the fact that Hyposulphite of Soda in presence of Chloride of Sodium is less active as a fixing agent, since the Chloride of Sodium exercises an opposing affinity and tends to keep the Silver in the state of Chloride.

For a reason similar to that above assigned, the fixing bath employed for Negatives should not be used for fixing positive prints, since the Iodide of Sodium present in the former tends to produce yellow patches on the surface of the print; which patches consist of Iodide of Silver in union with Albuminate of Silver or other analogous substances, and these compounds are very difficult of removal by the action of the fixing bath.

ON CERTAIN INJURIOUS CONDITIONS OF THE FIXING BATH.

The object of using the Hyposulphite Bath is to fix the proof by dissolving the unaltered Silver salts, without in any way affecting the image. But it is a fact familiar to the Photographic chemist, that the Hyposulphite of Soda, is a substance which very readily yields *Sulphur* to any bodies which possess an affinity for that element; and as the reduced Silver compound in the print has such an affinity, there is a tendency to absorption of Sulphur when the proofs are immersed in the Bath. Hence in many cases a sulphur-toning process is set up, and as the picture is improved by it in appearance, assuming a more purple shade, it is often encouraged by Photographers. Experience, however, has shown that colours brightened in this way are rendered less permanent, and therefore the careful operator will avoid sulphuration as far as possible. Some of the conditions which facilitate a sulphuretting action upon the proof, and are therefore injurious, are as follows:—

a. *The addition of an Acid to the Bath.*—It was at one time common to add a few drops of Acetic Acid to the fixing Bath of Hyposulphite of Soda, immediately before immersing the proofs. The Bath then assumes an opalescent appearance in the course of a few minutes, and, when this milkiness is perceptible, the print is rendered darker in colour. The chemical changes produced in a Hyposulphite Bath by addition of acid, may be explained thus:—The acid first displaces the feeble Hyposulphurous Acid from its combination with Soda. Then the Hyposulphurous Acid, *not being a stable substance when isolated*, begins spontaneously to decompose, and splits up into Sulphurous Acid—remaining dissolved in the liquid, and communicating the characteristic odour of burning Sulphur—and *Sulphur*, which separates in a finely divided state and forms a milky deposit. In chemical symbols, $S_2O_2 = SO_2$ and S.

Observe therefore that free acids of all kinds must be excluded from the fixing Bath, or, if inadvertently added, the liquid must afterwards be neutralized by Carbonate of Soda or Chalk.

b. *Decomposition of the Bath by constant use.*—It has long been known that Hyposulphite of Soda undergoes a peculiar change in properties when much used in fixing. The solution when first prepared leaves the image of a red tone, which is the characteristic colour of the reduced Silver Salt, but it soon acquires the property of darkening this red colour by a subsequent communication of Sulphur. Hence a simple fixing bath becomes at last a toning bath, without any addition of Gold. This change of properties has been shown by the Author to be due to a decomposition of Hyposulphite of Silver, and to the consequent formation of a sulphuretting body analogous in its properties to the Tetrathionates.* During the progress of the change Sulphide of Silver is thrown down, forming a black deposit, and the supernatant liquid becomes acid and effervesces on the addition of Chalk. The exact com-

* See *Journal of the Photographic Society*, September and October, 1851.

position of the acid body above mentioned as a product of the spontaneous decomposition of old fixing baths of Hyposulphite is not known, but the effects it produces on the prints are well understood, and can be shown to be most injurious; for it not only blackens the shadows of the picture by communicating Sulphur, but causes a loss of the middle tints, and destroys the pure white colour of the high lights.

In order to avoid the formation of this acid substance in the Bath, it is most important to wash away all the free Nitrate of Silver; hence arises one advantage of the alkaline Gold toning process over the old methods, since this process cannot be carried on unless the free Nitrate of Silver be first washed away. Another precaution is to keep the Bath shielded from a very strong light, and to put it away in a cool place: light and heat both favour the decomposition of Hyposulphite of Silver and cause a black deposit to be thrown down.

A more practical means of preserving a fixing bath for a long time in a state in which it communicates but little Sulphur to the proof is the addition of an *alkali*. The Author showed in his early papers on the Tetrathionates and their reaction with Hyposulphite of Soda, that alkalies decompose the unstable sulphuretting principle. Hence if the Bath be treated with Potash or Carbonate of Soda, an alkaline *Sulphide* is gradually formed, which precipitates Sulphide of Silver, and in the course of a few days the liquid returns to its original condition and ceases to act as a toning agent upon the proof. Here we see another point of excellence in the alkaline Gold toning process, since each print carries with it small doses of Carbonate of Soda, which effectually prevent the formation of acid in the Bath.

SECTION IV.

On the Fading of Photographic Prints.

For many years subsequent to the discovery of the process of Photographic Printing by Mr. Fox Talbot,

it was not generally known that pictures so produced were easily susceptible of injury from various causes, and in particular from traces of the *fixing-agent* remaining in the paper. Hence, due care not being taken in the proper cleansing and preservation of the proofs, the majority of them faded.

The present Section is intended to explain practically and in a concise manner the causes of the fading of Photographic Prints, and the precautions which should be taken to ensure their permanency.

a. *Imperfect Washing.*—This is perhaps the most important cause of fading and the most frequent. When Hyposulphite of Soda is allowed to remain in the paper, even in minute quantity, it gradually decomposes, with liberation of Sulphur, and destroys the print in the same way and quite as effectually as a solution of Sulphuretted Hydrogen or an alkaline Sulphide.*

Imperfect washing may be suspected, if the Photograph within a few months from the date of its preparation, *begins to get darker in colour:* the half-tints, which are the first to show the action, afterwards passing into the yellow stage, whilst the dark shadows remain black or brown for a longer time.

The proper mode of washing Photographs is sometimes misunderstood. The length of time during which the print lies in the water is a point of less importance than the continual changing of the water. When a number of Positives are placed together in a pan, and a tap turned upon them, the circulation of fluid does not necessarily extend to the bottom. This is proved by the addition of a little colouring matter, which shows that the stream flows actively above, but at the lower part of the vessel, and between the prints, there is a stationary layer of water which is of little use in washing out the Hyposulphite. Care should therefore be taken that the pictures be kept as far as possible

* The reason why the long-continued action of Sulphur fades the print, has already been indicated at p. 240. It is because the amount of real Silver in the image is very small, and Sulphide of Silver in minute quantity appears pale and yellow.

separate from each other, and when running water cannot be had, that they be frequently moved and turned over, fresh water being constantly added. When this is done, and especially if the *size* be removed from the paper in the manner presently to be advised, four or five hours' washing will be sufficient. It is a mistake to allow the pictures to remain in the water for several days; which produces no good effect, and may tend to encourage a putrefactive fermentation, or the formation of a white deposit upon the image when the water contains Carbonate of Lime.

Mr. Maxwell Lyte states that traces of soluble Chloride left in the paper are injurious to the permanency of Photographic prints: this indicates the propriety of avoiding the use of water too highly charged with saline matter, and of finishing the washing with a bath of rain-water.

b. *Atmospheric Oxidation.*—Upon examining collections of old Photographs, it is not uncommon to find prints which are stated to have remained unaltered for a long while after their first production, but which in the course of time have lost their brilliancy, and become pale and indistinct. This kind of fading often commences at the corners and edges of the paper, and works inwards towards the centre; it is principally caused by a slow process of *oxidation.*

Sulphuration in the process of toning, which has before been shown to occur when old and decomposed solutions of Hyposulphite of Soda are employed, always facilitates subsequent oxidation and yellowness. It is indeed difficult to avoid *slight* sulphuration unless fresh solutions of Hyposulphite are employed in fixing, but the remarks now made on the injury caused by Sulphur refer to its full action.

Moisture greatly hastens the yellow change due to atmospheric oxidation, and hence a state of comparative dryness may be said to be essential to the preservation of all Photographs. In collecting evidence upon the subject, "wet" and "damp" are frequently alleged as

having been causes of fading;—the prints were hung against a damp wall during frosty weather, in a room without a fire; or the rain had been allowed to penetrate the frame!

Acid matters, and also other bodies which dissolve Oxide of Silver, such as Ammonia, &c., favour oxidation when left for a long time in contact with the image. The materials often used in sizing papers, such as Alum and Resin, being of an acid nature, are ultimately injurious to the image; and the removal of the size, which may easily be effected by means of hot water, without much injury to the tint, has the additional advantage of carrying out the last traces of Hyposulphite of Soda, and also the germs of *fungi*, which, if allowed to remain, would vegetate and produce a destructive mouldiness.

The fact that acids facilitate oxidation of the image suggests also that Photographic Prints should not be handled too frequently, or touched with the finger more than is necessary; the warm hand may leave behind a trace of acid* which would tend in time to produce a yellow mark. For the same cause they ought not to be laid down carelessly in any place likely to communicate impurity.

The employment of albuminized paper confers a positive advantage in protecting the image from oxidation: this was proved by careful experiments performed with various oxidizers. The use of Albumen indeed gives the main chance of preventing a print which has been toned to blackness by sulphur, from gradually becoming pale and yellow by atmospheric oxidation.

c. *Improper Modes of Mounting the Proof.*—This cause of change might have been included with the last, since the fading of badly mounted prints is usually due to atmospheric oxidation. All cements which are of an acid nature, or which are liable to become *sour* by

* This acid reaction of perspiration is due to Lactic, Acetic, and Formic Acids.

acetous fermentation, should be avoided. Flour paste is especially injurious, and many cases of fading have been traced to this cause. The addition of Bichloride of Mercury, which is often made to prevent the paste from becoming mouldy, still more unfits it for Photographic use. No substance appears better than Gelatine, which does not readily decompose, and shows no tendency to absorb atmospheric moisture. The *deliquescent* nature of many bodies is a point which should be borne in mind in mounting Photographs, and hence the use of a salt like *Carbonate of Potash*, which the Writer has known to be added to paste to prevent the formation of acid, would be unadvisable.

d. *The Effect of Imperfect Fixation.*— The earlier Photographers did not always succeed in properly fixing their prints, and old Photographs are often found thickly studded with spots and blotches in the tissue of the paper. These prints, however, are not invariably faded upon the surface, and hence it cannot be said that imperfect fixation will certainly end in the total destruction of the picture. Still a notice of the subject may properly be introduced in this place, and the attention of the reader be once more drawn to the importance of examining each print by holding it against the light: imperfect fixation will be shown by yellow patches in the body of the paper.

e. Mr. Spiller has shown that Hyposulphite of Soda is not a perfect solvent of Albuminate and some other organic compounds of Silver. Hence some of these must remain in the paper in spite of all care taken to the contrary, and may be acted on by the air in a manner similar to that described in the next paragraph.

f. *Impurities in the Air.*—A Photograph carefully prepared may suffer injury from deleterious matters often present in the atmosphere. The air of large cities, and particularly that emanating from sewers and drains, contains Sulphuretted Hydrogen, and hence articles of silver-plate become tarnished unless placed beneath glass. The injury which a print sustains

by exposure to air contaminated with Sulphuretted Hydrogen, is less than the tarnish produced upon the bright surface of a silver-plate; but it is recommended as a precautionary measure, that Photographic Pictures should be protected by glass or kept in a portfolio.

The products of the combustion of coal-gas are probably more likely than the cause last named, to be a source of injury to Photographs suspended without any covering. The sulphur compounds in gas burn into Sulphurous and Sulphuric Acid, the latter of which, in combination with Ammonia, produces the sparkling crystals often observed upon the shop windows.

The question as to the manner in which the Photographic image may best be protected from these extraneous causes of fading has been mooted, and many plans of coating prints with some impervious material have been devised. If the pictures are to be glazed or kept in a portfolio, this of itself will be sufficient, but in other cases it may perhaps be useful to apply a layer of spirit or gutta-percha varnish. The use of wax, resin, and such bodies is likely, by introducing impurities, to act injuriously rather than otherwise.

g. *Decomposition of Pyroxyline a source of injury to Collodion Photographs.*—Although the present Section refers more especially to Photographic prints on paper, yet a few remarks upon Collodion images may not be out of place. Collodion Positives and Negatives are usually esteemed permanent; but some have been exhibited which, having been put away in a damp place, gradually became pale and indistinct. The change commences at rough edges and isolated points, leaving the centre, as a rule, the last affected. On examination, numerous cracks are often visible, thus indicating that the Collodion film has undergone decomposition, and has liberated corrosive Oxides of Nitrogen. Substitution compounds containing Peroxide of Nitrogen are known to be liable to spontaneous change. The bitter resin produced by acting upon white sugar with Nitro-sulphuric Acid, if not kept

perfectly dry, will sometimes evolve enough gas to destroy the cork of the bottle in which it is placed; the solution of the resin has then a strong acid reaction, and rapidly fades an ordinary Positive print.

These facts are interesting, and indicate that Collodion Pictures, containing in themselves the elements of their destruction, should be protected from moisture by a coating of varnish.

Comparative Permanency.—The Photographic prints do not *necessarily fade*, in the same manner as fugitive colours, by a simple exposure to light and air. Bottles containing Photographs suspended in damp air were placed outside the window of a house with a southern aspect, for nearly three months, but no difference whatever could be detected between Positives so treated and others kept in total darkness. Supposing a case, however, which is the common one, of injurious influences which cannot altogether be removed, it may be useful to inquire what mode of printing gives the greatest amount of stability.

Positives produced by a short exposure to light, and subsequent development with Gallic Acid, may be expected to be more permanent than ordinary sun-prints; not that there is any reason to suppose the chemical composition of a developed image to be necessarily peculiar, but that the use of Gallic Acid enables us to increase the intensity of the red picture first formed, and to add to its stability by precipitating fresh Silver upon it. This point has not always been attended to; it has been recommended to remove the print from the developing solution whilst in the *red* and early stage of development, and to produce the dark tones subsequently by means of gold; but this plan, although giving very good results as regards colour and gradation of tone, appears to lessen the advantage which would otherwise accrue from the adoption of a Negative process, and to leave the picture, as regards permanency, much in the condition of an ordinary print obtained by direct action of light.

The original Talbotype process, in which the latent image is formed upon Iodide of Silver, produces, next to Collodion, the most stable image; but the difficulty of obtaining bright and warm tints on Iodide of Silver, will stand in the way of its adoption.

Great stress has been laid upon the superior permanency given by the use of gold in toning, but the fact appears to be that the Gold is precipitated in so small a proportion upon *the lighter shades* of the proof, that it cannot be expected to preserve them from any destructive agencies. It will be sufficient if the toning and fixing can be fully effected without any real injury from communication of Sulphur.

The prints which are *least stable* are such as have been toned in *acid Hyposulphite Baths, without Gold;* and the difficulty of preserving such pictures from becoming yellow in the half-tones is very great. All those plans of toning in which Acetic or Hydrochloric Acid is mixed with Hyposulphite of Soda, and the Positive immersed whilst the liquid is in a milky state from precipitation of Sulphur, ought studiously to be avoided.

Mode of Testing the Permanence of Positives.—Permanganate of Potash in very dilute solutions and slightly acidified with Sulphuric Acid, is a very delicate test for Hyposulphite in the droppings from the corner of a print; a mere trace will instantly destroy the red tint of the solution.

A dilute solution of this Salt, prepared by dissolving half a grain, or from that to two grains, of the salt, according to its purity, in one gallon of distilled water, affords a convenient mode of testing Positives as regards their power of resisting oxidation. The Positives must be moved occasionally, as the first effect is to decolorize a portion of the liquid, the permanganate oxidizing the size and organic tissue of the paper. After an immersion of twenty minutes to half an hour, varying with the degree of dilution, the half-tones of the picture begin to die out, and the full shadows become darker

in colour. The bronzed portions of the print withstand the action longer, but at length the whole is changed to a yellow image much resembling in appearance the Photograph faded by Sulphur.

The most available and simple plan of testing permanence is to enclose the pictures in a stoppered glass bottle with a small quantity of water. If they retain their half-tones after a course of three months of this treatment, and do not become mouldy, the mode of printing followed is satisfactory.

Boiling water will also be found useful in distinguishing the unstable colours produced by Sulphur from those following the judicious employment of Gold; in all cases the image will at first be reddened by the hot water, but if toned without Sulphur it will, as a rule, recover much of its dark colour on drying.

A solution of Chromic Acid may also be applied to distinguish prints toned by Sulphur from others toned by Gold; the presence of metallic Gold protecting the shadows of the picture in some measure from the action of the acid.

The solution should be prepared as follows:—

Bichromate of Potash	6 grains.
Strong Sulphuric Acid . . .	4 minims.
Water	12 ounces.

The characteristic appearance of prints which have been much sulphuretted, and are very liable to fade, should be known. A yellow colour in the lights is a bad sign; and if the half-tones are at all faint and indistinct, with an aspect of commencing yellowness, it is almost certain that the Positive will not last for any considerable length of time.

CHAPTER X.

THE PHOTOGRAPHIC DARK ROOM.

This is the room in which the sensitizing of Collodion paper, &c., and also the development of the image, is carried on. It need not be *dark* in a visual, but only in a chemical sense. We have already seen that only certain rays of Light exercise a chemical effect on our sensitive compounds, hence it will be necessary to prepare them in a room so lighted as not to affect them. This may be done by lighting it with orange-coloured glass, and not working too close to the window. Red glass would be a more effective substitute, but as the working in that kind of light is exceedingly painful to the eyes, the other kind of glass is preferable. A lamp or candle for illumination is sometimes used, but as the rays proceeding from these are often of a very actinic nature, the direct light should be prevented from falling on the sensitive film, by interposing near the source of light a screen of orange-coloured glass. It is very easy to test the "dark room" for chemical rays, and if this has been once done when the external light is very powerful, no more testing will be necessary. Sensitize a Collodionized plate in a Nitrate bath, both of which are known to be in good condition. Expose the plate for a few minutes to such Light as may find access therein. Pour on a developer and watch if there be any reduction of Silver or darkening of the film. Should reduction take place, even to a small extent, it is probable that some actinic light, which might be troublesome, does exist in the room. But it is not always safe to conclude that such may be the cause of darkening, because the chemicals themselves may be in fault. Test again by a method, which although a little more troublesome, will infallibly point out the source

of *fogging*. Excite a Collodionized plate in the Nitrate bath, and immediately place it in a *dark frame*. Pull out the slide gradually within the dark room at intervals of, say, one minute intervening between each. Ten intervals may be selected, which would represent in the maximum ten minutes exposure to one minute in the minimum. A small portion of the plate should be left non-exposed.

Apply the developer, and watch closely for the following effects:—

1st. If the film remains clear all over, then in all probability the chemicals are right, and also the dark room is sufficiently protected from actinic rays.

2nd. If regular steps of gradation of darkening take place then the dark room and chemicals are certainly right, provided, as before, no deposit whatever takes place on that portion of the plate non-exposed in the slide.

The Photographic dark room should be well ventilated, otherwise the continued breathing of the pent-up fumes of Ether, &c., by the operator would eventually be prejudicial to health. It must be provided with a water tap and sink, or, where these are not available, with a large pouring jug and basin for the reception of washings, &c.

No chemicals should be admitted therein which are not necessary for the purposes of sensitizing, developing, &c., a wet Collodion plate. And as the photographer is necessarily working in a feeble light it is useful to have the various solutions placed not only in different positions, but also in different shaped bottles, so that the operator by the sense of touch alone can put his hand on the solution required. Above all things, Ammonia must not find a place within a dark room intended for the wet Collodion process, because the fumes from it very quickly destroy a Nitrate bath, and in the development are very prejudicial.

With these preliminary observations we are now in a position to proceed with practical work.

CHAPTER XI.

FORMULÆ FOR NEGATIVE SOLUTIONS.

1st. *The Plain Collodion.* Take of—

Ether, sp. gr. ·725	10 fluid ounces.
Alcohol, sp. gr. ·805	5 „ „
Pyroxyline	120 grains.

As before directed shake up the Pyroxyline in a bottle with the alcohol, then add the ether, and again shake till all the Pyroxyline that will dissolve has passed into solution.

2nd. *To Bromo-iodize the above Collodion.* Take—

Iodide of Ammonium . . .	40 grains.
„ Cadmium	40 „
Bromide of Cadmium. . . .	20 „
Alcohol, sp. gr. ·810 to ·815 .	5 fluid ounces.

Shake in a clean bottle till dissolved, and add to the above proportion of plain Collodion; or the Bromo-iodizing salts may be dissolved along with the Pyroxyline in the stock bottle. But in this case the formula will be slightly altered, and stand thus—

Ether, sp. gr. ·725	10 fluid ounces.
Alcohol, sp. gr. ·805 to ·815 .	10 „ „
Pyroxyline	120 grains.
Iodide of Ammonium	40 „
„ Cadmium	40 „
Bromide of „	20 „

Put the Bromo-iodizing salts first into the bottle, then add the Alcohol and afterwards the Pyroxyline. Shake well up until the salts are dissolved, complete

solution being much favoured by the rubbing action of the Pyroxyline. Lastly add the Ether, and again shake until all that is soluble of the Pyroxyline has been taken up. This is the plan which the writer invariably adopts in his own practice.

As the Iodide and Bromide of Cadmium are exceedingly stable salts when exposed to the vicissitudes of temperature, etc., and even in the presence of acids (although when used alone they are apt to render Collodion too viscous), they are of immense value in correcting the tendency which other Iodides, etc., have to undergo decomposition when dissolved in Collodion.

Various other formulæ for Bromo-iodizing Collodion for negatives have been proposed to suit different conditions of light, temperature, etc., but the above may be considered excellent for a good normal Collodion suitable for general purposes. If the heat of the weather and also the light are very intense, more Bromide may be used with advantage, probably because Bromide of silver is less liable than the Iodide to be over-acted on by strong impulses of bright light and by high temperature.

As a rule, Bromo-iodized Collodion is best adapted for an iron developer, but occasionally a Pyrogallic developer is used when the finest possible deposit of silver is required. The latter developer, however, acts with less energy than iron, and therefore a longer exposure is required.

Simply Iodized Collodion.—To each fluid ounce of the plain Collodion formulated in last page, add three fluid drachms of either of the following solutions—

Formula No. 1. (*Potassium Iodizer.*)

Iodide of Potassium	135 grains.
Alcohol, sp. gr. ·816	10 ounces fluid.

Pulverize the iodide, dissolve by agitation in a bottle, and filter if necessary. Solution is much assisted by placing the bottle for a short time in warm water, say

about 120° Fahr. If the Alcohol be too strong, all the Iodide will not be dissolved.

FORMULA No. 2. (*Cadmium Iodizer.*)

Iodide of Cadmium	170 grains.
Alcohol, sp. gr. ·810 to ·816 .	10 ounces fluid.

By agitation this Iodide will dissolve readily in the cold.

FORMULA No. 3. (*Mixed Iodizer.*)

Iodide of Ammonium	60 grains.
Iodide of Cadmium	90 „
Alcohol, sp. gr. ·810 to ·816 .	10 ounces fluid.

By agitation these Iodides will also dissolve readily in the cold.

Remarks on Formula No. I.—In the earlier days of Photography, this is the one which was generally used; but as the Collodion iodized with it is very apt after a short time to turn red by the liberation of free Iodine, which renders the Collodion less sensitive, it is recommended to iodize only a small quantity of Collodion at one time.

This iodizer usually remains colourless if kept in a dark place, but on exposure to light a trace of Iodine is liberated, tinging the solution yellow. On again removing the iodizer from the action of light, reabsorption of the liberated Iodine generally takes place.

Remarks on Formula No. II.—This is the most stable of all iodizing solutions; and the only drawback to its general use is its tendency to render the Collodion glutinous, and thus preventing the possibility of an even coating of Collodion on large plates in warm weather. It exhibits no tendency to decomposition either when in alcoholic solution, or when mixed with plain Collodion, hence, as in the next formula, it is used to correct the opposite tendencies of another Iodide.

Remarks on Formula No. III.—No Iodizer equals this for general utility. Collodion when Iodized with the Ammonium salt alone speedily decomposes, although at first the Collodion works remarkably well. In the formula, the proportion of Cadmium has been so arranged, from careful experiment, as to correct the tendency to decomposition of the other salt, even in the hottest weather. A light sherry colour after a time is imparted to the Collodion, which will remain constant for many months, even in the presence of a slight amount of acid, or in bright daylight.

Another variety of Iodizer similar to the last may be made by mixing equal parts of Formulæ Nos. 1 and 2.

THE NITRATE BATH FOR NEGATIVES.

1*st. For Bromo-iodized Collodion*—

Pure Nitrate of Silver	35 grains.
Distilled Water	1 ounce.

Make in the above proportions the required quantity of solution and iodize it as directed at p. 178. If the solution be neutral to test paper, that is to say, if blue litmus-paper immersed in it is not changed in colour after, say, fifteen seconds immersion, it is quite certain that the Nitrate bath in this state will not yield Negatives free from fog, unless the Collodion has become quite red by the liberation of free Iodine. But as such Collodion is very insensitive, and soon disorders the bath, it is better not to use it.

To rectify the solution, pour it into the glass bath or trough, and, supposing we have twenty ounces of solution, thoroughly stir up with it four drops of dilute Nitric acid (equal parts strong acid and distilled water) and test again with litmus-paper. After a few seconds the blue colour of the paper will probably assume a slightly reddish hue. If so, the solution may be fit for work. That fact, however, can only be ascertained by a practical trial with a Collodion known to be good. If

the developed Negative is not free from a deposit of silver in the deepest shadows where light has not acted, or from *fog*, as it is technically called, add two more drops of dilute acid and try another plate. Most likely a nice blooming Negative will be the result. If not, try the effect of another drop or two of acid.

The operator, however, must be very careful not to add too much acid, which has the effect of diminishing the sensitiveness of the film, and at the same time giving a very feeble image. For this reason the writer recommends, and in his own practice invariably adopts, this progressive and tentative method of acidulating the Silver bath.

If by inadvertence too much acid has been added, there are two ways of remedying the mistake. By far the best plan is to add to the bath by degrees some Nitrate solution of the same strength, which has not been acidulated, practically testing with plates, as before, between each addition.

The second and more troublesome plan consists in correcting an over-acid bath with Oxide of Silver. Proceed thus. Dissolve say five grains of caustic Potash or Soda in an ounce of water, add to this a solution of Nitrate of Silver till no more precipitate falls. The precipitate is Oxide of Silver. Whilst still freshly made, throw the whole into a filter till the liquid has run through. Afterwards wash the precipitate by passing through the same filter two or three ounces of distilled water. This, besides washing away impurities, will dissolve a little of the Oxide, but the small quantity dissolved is of no consequence. Next pass the over-acid silver solution through the same filter, when it will be found that the acid has dissolved a considerable portion of the Oxide, and the filtered solution will now, when tested with litmus-paper, be found to be neutral, or perhaps slightly alkaline. Try it as before with collodionized plates, and correct more carefully this time with dilute Nitric acid.

2nd. *For Iodized Collodion—*

Pure Nitrate of Silver	30 grains.
Distilled Water	1 ounce.

Dissolve and Iodize as before.

It will sometimes be found that this sensitizing solution works very well for Iodized Collodion without any addition of acid. In this respect much depends on the Collodion. A sample of Collodion which has become highly coloured by the liberation of free Iodine, works best when excited in a neutral bath; but it is obvious that a Nitrate solution cannot long remain neutral if films containing free Iodine are sensitized in it, because the Iodine combines directly with the silver, liberating the Nitric acid, which having no displaced base wherewith to combine, renders the solution more and more acid by the sensitizing of every successive plate. Such Collodions, when much discoloured, should not be used, as they invariably and quickly injure the bath. To acidulate the sensitizing solution for a good Iodized Collodion the best acid to use is the Acetic, and it should be added tentatively, as described in the instructions for acidulating the bath for Bromo-iodized Collodion (see p. 207).

TO PRESERVE THE NEGATIVE AND POSITIVE BATHS FOR COLLODION.

The following observations apply both to the Nitrate solutions for Negative and Positive processes by means of development :—

By dipping successively a large number of Collodionized plates into a bath, the silver solution becomes changed in various ways.

1st. The water absorbs some of the Ether and Alcohol which still remain in the immersed film.

2nd. When the Iodine, Bromine, &c., of the Collodion combine with the Silver, a corresponding quantity of Cadmium, Potassium, or whatever other metal is

combined with the Haloid salt, is set free, and combines in its turn with the liberated Nitric acid, forming Nitrates of these metals, which remain in solution. These secondary Nitrates are not hurtful to the Bath, farther than that they weaken its power for sensitizing.

3rd. With every successive plate there is introduced into the Silver bath a greater or less amount of organic matter. This is partly derived from the fingers whilst handling the plate, and partly from the Collodion itself. Nitrate of silver has a great affinity for these organic substances, and consequently the bath is liable after a time to become loaded with dissolved matter which is fatal to the production of a clearly defined Negative or Positive, unless controlled by a great deal of Nitric or Acetic acid. This remedy necessitates a very much longer exposure, which, for Portraits at least, is not admissible.

4th. One of the most potent destroyers of a Negative or Positive bath for Collodionized plates is the formation therein of Nitro-iodide or Nitro-bromide of Silver. It will be necessary to explain this phenomenon shortly, as the facts have now been fully ascertained and the causes traced to their sources.

When an Iodized, Bromo-iodized, or Bromized Collodion film is being sensitized in the Silver bath, the first effect of the silver is to convert the soluble Iodide, &c., into the corresponding salts of silver. When that is completed the excess of Nitrate of silver begins to dissolve out or destroy its own offspring. After a time the Nitrate becomes saturated, and then the new compound crystallizes out in fine needle crystals in the Nitrate bath, or more generally in the Collodionized film. Alcohol and Ether in the bath much favour the deposition of these crystals, which are insensitive to Light and constitute one of the most fertile causes of *pin-holes* or transparent spots in Negatives. Simply Iodized Collodion is less liable to this influence than a Bromo-iodized.

If the Nitrate bath is otherwise working well, the

best remedy is to add to it say one-third of its bulk of distilled water, which will throw down a large proportion of the Iodide and Bromide which it has taken up. Filter and then dissolve in it Nitrate of Silver in proportion to the quantity of water added. Acidulate if necessary.

With reference to an excess of organic matter in the Nitrate bath, the best way to test for failure in that direction is to take a portion of the solution and make it slightly alkaline with Ammonia. If by exposure to strong light the liquid does not become turbid after two hours, then organic matter is not present in excess. This reducing power of Light on solutions of Nitrate of silver containing organic matter is taken advantage of to purify them. Proceed thus. Pour the impure bath into a *transparent* wide-mouthed bottle, add Ammonia drop by drop till reddened litmus indicates, by becoming blue, that the solution is *slightly* alkaline. It is better not to stopper or cork up the bottle, as it is important to allow any Ether or Alcohol which the solution contains to escape. Dust may be kept out by placing loosely over its mouth a conical fold of thin blotting paper after the manner of a candle extinguisher. This does not materially interfere with the escape of vapour. The vessel is now placed in sunlight or strong diffused daylight, in a place where rain does not find access to the interior. After a few days' exposure most of the organic matter will be precipitated and reduced, in combination with part of the silver, to a black powder. The time of reduction varies, according to the intensity of the Light and the amount of Organic matter present, from five to thirty days. The bath should now be filtered, but if it is an old one fully saturated with Iodide and Bromide of Silver, it is better before filtering to add to it say one-third of its bulk of distilled water, the effect of which is to precipitate a portion of these salts in an extremely fine state of division, which will pass through a very porous filter. If, however, the weakened silver solu-

tion is well agitated and allowed to stand for a day or so, the particles will agglomerate and fall to the bottom. The solution should now run through the filter perfectly clear.

To render the bath again fit for work, dissolve in it pure Nitrate of Silver in the proportion of thirty-five grains Nitrate to each ounce of distilled water used in diluting. Acidulate it either with Nitric or Acetic Acid as previously directed in making a new bath.

Such solutions, when the corrections have been properly made, work quite as well as new ones.

CHAPTER XII.

MANIPULATIONS OF THE WET COLLODION PROCESSES.

CLEANING THE GLASS PLATES.

In selecting glass for Photography care should be taken. Common window glass will answer well enough for Positives taken direct in the Camera; but for Negatives it is not sufficiently flat, and is liable to break when screwed into the pressure-frame for printing. What is called "flatted crown" will suit for small Negatives, but unfortunately it is not always flat, and therefore a risk is run of its breaking when large sheets are used. "Patent plate," although much more expensive, answers better than any other kind of glass, especially for large sizes, and as it is perfectly flat no risk is run of its being broken in the Printing-frame if grit or sand is not interposed between the two glasses.

Before washing the glasses each piece should be roughened on the edges and at the corners, by passing round them a sharp file, or more quickly by making two plates do duty for each other. Hold their edges at an angle, taking care to keep the arms fully extended, to prevent spiculæ from flying off into the eyes, then successively draw the edges sharply along each other. This will be a sufficient protection to the hands from sharp edges.

It would not be safe to rely on glass being photographically clean by washing it in water, and then wiping it with clean cloths or wash-leathers. There are often impurities on the glass which these will not

remove. The safest way is to proceed methodically, by a plan which will insure a clean glass, if the glass itself contains no internal contaminations, which by oozing out might affect the Photographic Chemicals. Make a mixture consisting of one part of Hydrochloric Acid and four parts common water. Lay the plate down on two or three folds of flannel laid on a flat table. With a dabber, which may conveniently be made of a *bung* or large cork, wrapped round with chamois leather, rub over the surface of the glass with considerable pressure a few drops of the Hydrochloric mixture. Wash off the acid under a tap, finally rinsing with distilled or filtered rain-water, and rear up the plates to dry in a place free from dust; of course taking care to mark a corner of the cleansed side by any device which may be deemed most convenient. These glasses are ready for use at any time in the wet Collodion process, by simply brushing off with a broad camel's-hair brush any dust that may have settled on the prepared surface.

Another method of cleaning Photographic glass which has not been previously used is very efficacious.

Drop on the surface to be coated with Collodion a few drops of old Collodion, thinned with Ether or Alcohol, or preferably Tincture of Iodine. Instantly with a dabber, kept for that purpose alone, energetically work over the surface of the plate till the liquid has been rubbed off or has evaporated. Breathe on the plate, and with a fresh dabber or leather instantly rub off the condensed moisture. The glass is ready for use when, by again breathing on it, the condensed moisture evaporates regularly and not in patches.

The cloths or wash-leathers used for wiping Photographic glass should be kept expressly for that purpose. The cloths are best made of a material known as fine "diaper," and very free from flocculi and loosely adhering fibres. Wash them by soaking them for a night in a tolerably strong solution of common washing Soda. Wring them out and wash them out in several changes

not less than ten of clean water; wring between each change, then hang up to dry. Wash-leathers are similarly prepared, but here the operator must be careful not to use warm water, as that would shrivel up the skins. They must be washed till all the Soda and "dressing" has been removed. It will take longer to remove the latter than the former, but as the dressing is insoluble in water, it is easy to see when the whole of it has been washed away. These leathers when dry are generally harder and less pliant than they ought to be. In that case roll them up into a ball, and beat them with a wooden mallet till they become soft and pliant.

Silk handkerchiefs for finally polishing the dry plates are not recommended, because in particular states of the weather the glass by being rubbed with them becomes strongly electric, and attracts any dust which may be floating in the immediate neighbourhood. Chamois leather does not electrically excite the glass so powerfully, and therefore is to be preferred.

To Clean Plates that have been previously used.—If on developing a plate the picture is considered a failure, it is best to wash off the Collodion, &c., at once and set aside to dry, when the glass may be considered as good as new. But if the Collodion film has been once allowed to dry, it is better to soak the glass for some time in a solution of common Soda and wash as before.

If the glass plate has been varnished, soak it for a night in a very strong solution of Soda, when probably the film and varnish after a little rubbing will break away in patches. But some sort of varnishes resist this treatment. They must, however, give way to the extraordinary solvent power of Pyroxylic spirit, or Wood Naphtha. To apply this solvent, lay the plate on a flat table, pour a little of the spirit on the varnish, rub with a dabber, when varnish and Collodion will both quickly be detached from the glass. These plates should then be soaked in Soda and washed as before.

Strong acids too have a similar effect, and act very

quickly. The writer, who in his practice with his students has often occasion to make Pyroxyline, and finds on his hands at the end of a year a large number of varnished negatives which are of no use, preserves the Nitro-sulphuric acid which has already served its original purpose. Into this the varnished plates are dipped one by one, by means of a glass dipper or clip, or a number of them are allowed to soak in the mixture of acids for a short time. When placed in water, the films are easily rubbed off. This plan is recommended only to those who have plenty of waste acids which otherwise would be thrown down the sink without doing this final service.

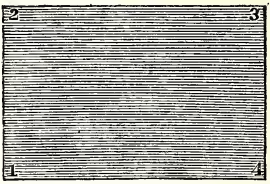
General Remarks on Cleaning Glasses.—Much time is often wasted in finally cleaning glasses for the reception of the Collodion by the operator's frequently breathing upon them violently, and thus projecting particles of saliva which requires a great deal of rubbing for removal. Gentle breathing is all that is required. Again, the condition of the cleaning cloths or leathers for finishing should be carefully attended to. They should never be touched with moist hands, or hands contaminated with chemicals, and when not in use they should be stored away in a clean cotton bag, and in a dry place.

TO COAT THE PLATE.

When the salted Collodion has settled for some days decant off a portion into a pouring bottle for use, taking care not to disturb the sediment. The best, and at the same time cheapest, pouring vessels are the tall *lipped* medical bottles, procurable at any druggist's. They must be fitted with the best corks so as to prevent the evaporation of the Ether and Alcohol. Now take a glass plate, previously cleaned, and wipe it gently with a broad camel's-hair brush, in order to remove any particles of dust which may have subsequently collected. If it be a plate of moderate size, it may be held by the corners in a horizontal position, between

the forefinger and the thumb of the left hand. The Collodion is to be poured on steadily until a circular pool is formed, extending nearly to the edges of the glass.

Fig. 10.



By a slight inclination of the plate the fluid is made to flow towards the corner marked 1 in the above diagram, until it nearly touches the thumb by which the glass is held; from corner 1 it is passed to corner 2, held by the forefinger; from 2 to 3, and lastly, the excess poured back into the bottle from the corner marked No. 4. It is next to be held over the bottle for a moment, until it *nearly* ceases to drip, and then, by raising the thumb a little, the direction of the plate is changed, so as to give a rocking movement, which makes the diagonal lines coalesce and produces a smooth surface. The operation of coating a plate with Collodion must not be done hurriedly, and nothing is required to insure success but steadiness of hand and a sufficiency of the fluid poured in the first instance upon the plate.

In coating larger plates, the *pneumatic* holder, which fixes itself by suction, will be found the most simple and useful.

The presence of white light in the room does no injury until the plate has been placed in the Bath, and therefore the door may remain open during the operation of coating, since it would be difficult to apply the fluid evenly without plenty of light. Draughts of air, however, must be avoided as much as possible, since they promote too rapid evaporation, and carry along particles of dust which may adhere to the plate. If the

dark room is illuminated by a yellow flame from a tallow candle or by a whiter flame surrounded with orange glass, be careful not to Collodionize the plate near these, nor to have an open bottle of Collodion near them, because, as the vapours of Ether and Alcohol are very inflammable, disastrous consequences might ensue.

Sensitizing the Film.—As soon as the Collodion on the glass plate has *set*, as it is called, or when by touching the draining corner the drop of Collodion does not adhere to the finger, and this time, according to temperature, &c., may vary from ten seconds to a minute, the plate is rested on the glass dipper and lowered into the solution by a slow and steady movement; if any pause be made, a horizontal line corresponding to the surface of the liquid will be formed. Then place the cover upon the vertical trough and darken the room, if this has not already been done.

Whilst the plate remains in the Bath, the operator may occupy himself in wiping out the corners and lower edge of the dark slide with blotting paper; next, in measuring a sufficiency of the developing solution, and in focussing the object. Then rinse the fingers an instant in water, to cleanse them from any traces of soluble impurity and return to the Bath.

The light ought to fall upon the plate at a sharp angle whilst it is lifted from the Bath, that the operator may see the greasy lines upon the surface. An immersion of from two to three minutes will usually be sufficient to remove them in warm weather; but when the temperature falls, the time must be prolonged. Something will depend upon the number of times the plate is moved up and down, and many adopt the plan of leaving it in five minutes, and then taking it out without any movement. When the liquid flows off in a uniform sheet, the decomposition may be considered to be perfect. The principal impediment in this part of the process lies in the difficulty with which Ether and Water mix together, which causes the Collodion

surface on its first immersion to appear *oily* and covered with streaks. By gentle motion the Ether is washed away, and a smooth layer obtained.

When the Nitrate bath is in perfect order no harm will result from leaving the plate in it for a longer time; but the experience of all practical Photographers points to the fact that nothing is gained by a prolonged immersion, and much clearness of image may be lost.

The plate is next drawn gently up through the solution, removed from the dipper and held vertically over the trough for a minute to drain. To farther drain the plate some operators rest the lower edge for a short time on a few folds of blotting paper, and also wipe the back with the same material. These latter precautions are, however, not necessary if the dark slide is furnished with a well or trough at the bottom into which the solution may run. The plate is now placed on the silver wires of the frame, taking care that the draining end be towards the bottom. *In carrying the dark frame to and from the Camera, and at all times when the plate is inside*, make sure that the slide is kept in such a position that no liquid can run back over the film. If this precaution be not attended to many sorts of defects will be visible in the picture. The frame too should be carried very gently, else particles of dust and abraded wood might be set loose and settle on the surface of the film. These would give rise to spots in the picture either of a transparent or opaque character, according to the nature of the impurity which causes them.

All the observations contained in this Chapter apply both to Collodion Negatives and Positives taken in the Camera. In the next two Chapters we must make a distinction between the two processes and describe them separately, because in some respects the treatment which is best adapted for the one will not suit the other.

CHAPTER XIII.

THE POSITIVE COLLODION PROCESS ON GLASS OR METALLIC PLATES (FERROTYPES).

We have previously detailed the various operations and chemicals necessary before obtaining a Positive picture by development—viz., cleaning the glass, the Collodion, the Sensitizing bath, the developers, the fixing agent, and the general observations contained in last Chapter. It now remains for us to describe those manipulations wherein the Positive process differs from the Negative. These consist mainly in the development.

In developing a glass Positive the solution of Sulphate of Iron should be flowed evenly over the film, and in some quantity, so as to wash off a portion of Nitrate of Silver into the sink. In the case of Negatives it is an object to save every trace of Nitrate, and precipitate it upon the image, in order to increase the density; but with Positives there is a fear of getting an excess of intensity, and if the Collodion film be tolerably creamy, it will always retain more than enough of the Nitrate to give a Positive free from the green or blue marks characteristic of deficient reduction. White stains at the margins of the plate are produced in great measure by the developer coming into contact with an excess of Silver.

Tilt the developing fluid backwards and forwards upon the film for about thirty seconds, or a minute, until the darkest shadows *begin* to be visible. Supposing the film to be well lighted with yellow light, there will be no difficulty whatever in ascertaining when the image is fully out; the developer must then be poured off immediately, and the plate washed with

water, or the image will be rendered too dense by fresh precipitation of Silver, and the middle tints in the face will be lost in consequence. The blacks are rarely quite pure when the plate has been too much developed, but show either little spangles of Silver, or a general clouding.

When the Sulphate of Iron is washed off before the proper development is complete, the whole image looks very thin and weak, with a blue or greenish tint: the details in the shadows may perhaps be visible, if the plate was fully exposed, but usually they are more or less defective. The difficulty, with the beginner, is to distinguish the effects produced by wrong exposure in the Camera, from others due to faulty development. A little care, however, will usually enable him to do so. If no details appear in the dark shadows, the image is either under-exposed or under-developed, but in the latter case the lights would be very poor and thin, as before described; whereas in the former they would probably be vigorous, especially if the operator kept the Sulphate of Iron for a long time upon the film with a hope of bringing out the shadows.

The finished picture in another case, the reverse of the last, may appear altogether too white and flat, without any deep shadows, every portion of the plate showing more or less of a deposit of Silver. In this instance it is either over-exposed or over-developed, but probably the former, and particularly so if the lights are not of a very good colour, but appear grey and feeble, *and if the whole image shows very fairly as a Negative when held against the light.* You may always calculate upon diminishing excessive density of the face and light parts by over-exposing in the Camera, but over-development makes them quite opaque, so that the black varnish, when placed beneath, does not show through. On the other hand, a prolonged exposure produces a far greater effect in clouding over the shadows, and giving a grey colour to black drapery, than any amount of over-development.

When all the Chemicals are in good working order, the finest Positives are obtained by giving a rather short exposure in the Camera, because the lights are then of a pure white, and the shadows transparent. With a Collodion not suitable for Positives, the image would be too intense when developed after a short exposure.

Wash the plate with water, to remove the whole of the Iron, before putting on the Cyanide, else a blue deposit will often be formed. The Cyanide may be used over and over again until exhausted.

In mounting glass Positives it has become a common practice to cover the back of the glass with black varnish, and to mount the picture with the Collodion side towards the eye. The image is necessarily reversed, but the whites are very bright, and the shadows sufficiently clear if the Collodion be of the transparent kind, and if the front is also varnished with a hard-drying transparent varnish, the image will not so readily fade away when thus protected from noxious fumes.

CHAPTER XIV.

THE NEGATIVE COLLODION PROCESSES ON GLASS.

SECTION I.

WITH IODIZED COLLODION.

The manipulations connected with cleaning, collodionizing, &c., the glass are the same as those described in the previous chapters; but the chemicals and the mode of using them differ in some respects.

As described in the last chapter, the glass having been cleaned, polished, and with a broad camel's-hair brush freed from adhering dust, is coated with iodized Collodion made by either of the formulæ at p. 266. When the film has *set* it is introduced by means of a glass dipper into the sensitizing bath made and corrected according to the formula at p. 206. Extreme care must be taken to introduce into this bath, along with the plate or otherwise, as little as possible foreign matter, such as that of an organic kind, inasmuch as Iodide of Silver *per se* is very much more liable to be disturbed in its action by such contaminations than are the mixed Iodide and Bromide.

When the plate is fully sensitized in the Nitrate solution, it is exposed in the Camera, usually for a longer time than that required for a Positive on glass, and the slide, with all convenient speed, removed into the dark room.

The image is developed by the following solution :—

Pyrogallic Acid	3 grains.
Distilled Water	1 ounce.
Glacial Acetic Acid	30 minims.
Or Citric Acid	2 grains.

In hot weather less Pyrogallic acid may be dissolved, if on trial it is found that the developer acts too energetically. Again, in cold weather the restraining Citric or Acetic Acid may be diminished if the development proceeds too slowly, but still leaves the image clear.

On taking the plate out of the slide there will be some accumulation of Bath solution at the lower edge, which, if the glass be held horizontally for a short time, will be seen to work its way along the surface of the film; and the effect will be to produce a *transparent* mark on applying the Pyrogallic acid. To prevent this annoyance, the film may be pressed vertically, for an instant, on absorbent blotting-paper, and the liquid drawn off by suction.

The Pyrogallic acid solution having been previously measured out (about three drachms for a plate 5×4, one ounce for a 9×7, and twelve drachms for a plate of 10×8), hold the glass in the hand in the same manner as when coating it with Collodion, and throw the liquid on evenly. It must not be poured from a height on to one single spot, or the whole of the Nitrate of Silver would be displaced from that spot, leaving a transparent mark of non-reduction. The lip of the developing glass should be depressed until it nearly touches the film, so as to apply the liquid close to the edge of the plate, or to some part of the image which is of minor importance. Always pour out the whole of the measured quantity of developer, and then move the plate so as to keep it waving backwards and forwards upon the film. It will be quite necessary to have the source of light so arranged that it falls nicely upon the Collodion surface, because the operator has to tilt the glass until the developer runs into each of

the corners, and to keep his eye upon the wave as it moves backwards and forwards, in order to prevent it from flowing off at the edges of the plate, or trickling down his sleeve.

The freedom with which the developer flows depends much upon the Collodion, and the length of time it was held before dipping, since if the film retain too much Ether it will repel aqueous liquids. It also depends upon the Bath in a measure, for when this solution is newly mixed, and comparatively free from Alcohol, it will be sometimes necessary to give the plate a sudden *jerk*, to prevent the Pyrogallic Acid solution from stopping short of the edge.

Notice whether the developer remains bright and clear, or becomes turbid before the image is fully brought out. In the latter case the heat is too high, or the chemicals are in fault, and the Chapter on "Failures" must be consulted.

Watch the course of the development for about thirty or forty seconds, and especially the behaviour of those parts of the film which at first remain yellow, but at length begin to evolve fine details corresponding to the shadows. Keep the Pyrogallic Acid on the plate until nothing more appears in these yellow parts, and then pour it off into a measure, and hold the plate for an instant against the light, so as to look through it and see the appearance of the Negative image.

At this point a failure very commonly occurs, from the operator being too tardy in his movements, and allowing the developer to run into oily lines, so as to produce diagonal black streaks upon the film.

Having decided that the image is sufficiently intense, proceed to the fixing; but if it appears too weak (and allowance must be made for the lowering action of the Hyposulphite), carry the development into the second stage. To do this, pour away the discoloured Pyrogallic Acid, and wash out the glass rapidly with water; then measure out a fresh portion, add to each drachm about five drops of a 20-grain solution of Nitrate of

Silver, and apply it a second time to the film, until the desired intensity is obtained.

It is not recommended to add a few drops of the Nitrate Bath to the Pyrogallic Acid, but to employ a weaker solution of Nitrate of Silver, not saturated with Iodide. This Nitrate of Silver must also be very pure, else the developer will soon discolour, and the shadows become stained.

As *time* ought to be economized as much as possible, observe the following:—If the image is well out before the Pyrogallic Acid becomes turbid, it will be unnecessary to throw away the first portion, but any amount of strengthening may be obtained by pouring the same developer back into the measure, and adding the Nitrate of Silver. Neither is it necessary to wash out the developing glass with water when it contains Pyrogallic Acid *simply discoloured*, but anything approaching *turbidity* will suggest an immediate change of solution, and a washing with water, both of the film and the glass. The addition of fresh Nitrate of Silver to a developer in such a state, is improper: the Silver then falls irregularly, and the chance of staining is increased.

With regard to the quantity of Nitrate of Silver to be added to the developer, nothing positive can be stated. At least three times as much will be required in cold as in hot weather, and something will depend upon the condition of the developer itself. The rapidity of discoloration or turbidity in the Pyrogallic Acid is the proper guide to follow; and the two liquids may be mixed even in equal bulks if it is found that the mixture remains clear for twenty or thirty seconds, so as to give time for pouring it over the image. As a rule, however, the less the quantity of silver in proportion to the Pyrogallic Acid the better.

Convenient dropping bottles can now be had at most of the Photographic warehouses, or a small thin-lipped phial may be used.

Appearance of the Negative image developed with Pyrogallic Acid as a guide to the exposure to Light.—An under-exposed plate develops slowly. By continuing the action of the Pyrogallic Acid the high lights *become very black*, but the shadows are usually defective, nothing but the yellow Iodide being seen on those portions of the plate. After treatment with the Hyposulphite, the picture shows well as a Positive, but by transmitted light all the minor details are invisible; the image is black and white, without any half-tone.

An over-exposed Negative develops rapidly at first, but soon appears to blacken slightly at every part of the plate. After the fixing is completed, the image is indistinct, and very little can be seen by reflected light but a uniform grey surface of metallic Silver. By transmitted light the plates often show a red or brown colour, and the image is *faint* and flat. The half-shadows having acted so long as nearly to overtake the lights, there is a want of proper *contrast;* hence the over-exposed plate is the exact converse of the under-exposed, where the contrast between lights and shadows is too well marked, from the absence of intermediate tints.

A Negative which has received the proper amount of exposure, usually possesses the following characters after fixing:—The image is partially but not fully seen by reflected light. In the case of a portrait, any dark portions of drapery show well as a Positive, but the features of the sitter are scarcely to be discerned. By transmitted light the figure is bright, and appears to stand out from the glass; the dark shadows are clear, without any misty deposit of metallic Silver; the high lights black *almost* to complete opacity.

Collodion with strong organic reactions gives a Negative which often shows upon the surface of the glass nearly as well as by transmission. And if the light be at all good, the yellow creamy appearance which Photographers term *bloom* ought to be seen

upon the image. Its absence in the case of a simply iodized Collodion, not containing Bromide, usually implies that some of the chemicals are out of order.

Fixing the Negative.—Fixing the negative, or in other words removing from it all the unaltered Iodide, is best done in the case of Pyrogallic developed images by a strong solution of Hyposulphite of Soda. Even a very weak solution of Cyanide of Potassium is apt to weaken the half-tones of such images on account of the exceedingly fine deposited particles of Silver, whereas strong Hyposulphite of Soda solution, unless allowed for a long time to act, exercises no such baneful propensities. The plate may be either dipped in the solution until the yellow appearance has disappeared, or the solution may be poured over the plate.

Washing the Negative.—This may be done in any place where there is abundance of water, only the washing must not be long delayed. The best place is under a tap running with a gentle stream—a violent stream would wash away the film altogether, and so would a gentle one if the still tender film is placed too far below it. Wash first the picture-side for a short time, and drain the superfluous water from a corner for an instant. Next do the same with the back of the plate, and allow the stream also to run over the fingers, to remove any soluble impurity resting on them; drain again, and for a minute at least let the water run on and off the picture-side. Finally, place the negative, slightly strutting, against a flat board, collodion side next the board (to prevent dust from attaching itself to the still soft and tender film), and resting on several folds of blotting paper, which absorbs the moisture as fast as it drains away, and prevents dust from creeping up by capillary attraction. In washing plates under a stream of water impinging on the films for the same time, there is a way of doing the operation thoroughly well and a way of doing it badly. Simply putting the plate under a stream of water or

soaking in any amount of water for a few minutes will not remove all the fixing solution. The plate must be *drained* or allowed to drip by holding it perpendicularly every now and then for a few seconds. In this way all the fixing solution can be removed with little water and less trouble in a very short time.

The writer has seen a pernicious practice adopted by some operators busily occupied in studios—viz., that of rearing up the newly fixed plates inside a large tub of water, leaving them to wash themselves whilst they were otherwise engaged. If a stream of water were running through the tub this plan would be effective; but if the water is not changed several times, such washing amounts only to a greater or less dilution of the fixing liquid, and consequently some portion of the fixing salt remains in the film, and eventually destroys the image.

SECTION II.

THE NEGATIVE PROCESS ON GLASS WITH BROMO-IODIZED COLLODION.

This is the process now generally adopted both for portraits and landscapes, inasmuch as there is less liability to failure from impurities of the chemicals; and not because the process itself possesses greater sensitiveness to luminous action.

The constitution of the Collodion has been given at p. 265, and of the Nitrate senzitising bath at p. 268. Here, also, the cleaning of the plate, the collodionizing, the sensitizing, etc., are the same; but the mode of development is somewhat different from the two processes already described.

The primary developing solution consists of:—

Protosulphate of Iron	15 grains.
Glacial Acetic Acid	30 minims.
Water	1 ounce.

Filter if there be any turbidity.

According to temperature this normal solution may advantageously vary in the proportion of its constituents. One constituent will alter all the rest, water being the most convenient.

In very hot weather, or when the developer acts with uncontrollable energy, weaken the solution by increasing the amount of water. Or, again, in cold weather, when Chemical action is less powerful, decrease the proportion of water.

The mode of applying this developer is the same as that given at p. 285. But since Iron, as a rule, acts more rapidly than Pyrogallic Acid, more manual dexterity is required in applying the solution so as to prevent unequal development.

It will seldom be found that sufficient density of negative can be obtained by the first development. A secondary stage, or reinforcement of the image, must therefore be had recourse to.

To effect proper density, the first developer is washed off—a slight rinse with water will be enough—and while the film is still moist, a fresh solution of Iron is poured into a clean cup, into which a few drops of Nitrate of Silver, acidulated with Acetic Acid, have been previously put. Instantly apply this mixture to the film, and spread evenly. Tilt the plate about gently to keep the solution in motion; after a few seconds pour the redeveloper back into the cup and look through the negative held up between the eye and the orange window or lamp of the dark room. If sufficient density of deposit is not manifested, rinse the film with water and again apply in the same way a fresh solution.

Mr. Wilson, of Aberdeen, who has been exceedingly successful in his Photographic practice, adopts a slightly different method of intensifying the image. After washing off the first developer, he applies to the film itself a few drops of Nitrate of Silver and redevelops with a fresh dose of Protosulphate of Iron.

Another mode of intensifying a feeble iron-developed

image is frequently adopted. This plan is very efficacious, and the only danger attending its adoption is the carrying of the redevelopment too far.

Pyrogallic Acid	1 grain.
Citric Acid	2 grains.
Distilled Water	1 ounce.

When the iron-developed image has been *well washed*, and before it has had time to dry, a few drops (more or less according to the size of the plate) of *Aceto*-acidulated Nitrate of Silver is stirred up with sufficient of the above Pyrogallic solution and poured on and off till by looking through the negative sufficient opacity of deposited silver has been obtained.

It must ever be borne in mind that all these reinforcing appliances, before the plate is fixed, must be made in the dark room, as the film is still sensitive to Actinic light.

The plate is now fixed in a weak solution of Cyanide of Potassium, or in a strong solution of Hyposulphite of Soda, and afterwards carefully washed, as already described, and set up to dry.

Intensifying after fixing.—It will sometimes be found after the finished Negative has been taken out into a strong light and examined, that the density of the deposit is not sufficient. In that case, take the plate back into the dark room before it has had time to dry, and reintensify by the Pyrogallic Acid formula and Silver. This may be done in daylight, but the developer decomposes more rapidly. No more perfect test than this for a thoroughly washed Negative can be found. If the fixing solution has not been entirely eliminated, brown patches will be developed in those places where the least traces of Hyposulphite of Soda or Cyanide still linger. Of course the plate must be again thoroughly washed and set up to dry on blotting paper.

VARNISHING THE NEGATIVE.

Before printing *positives* from the *negative*, it is essential that the latter should be varnished or protected

from injury, because a dried Collodion film is easily scratched, and is very absorbent of moisture, which would render it still more tender, or maybe detach the film altogether from the glass.

The composition of the best Photographic varnishes is by manufactures kept secret; but even were all the materials known, so much success depends on the method of compounding them that it would not be worth the Photographer's while to manufacture them on a small scale for his own use, as the most efficient kinds can be purchased cheaper and probably much better than he himself could make them. It is not recommended to use those varnishes which may be applied without first warming the negative, because it has been found that they afford a less efficient protection to the film than some others which require the glass to be heated.

Hold the picture-side of the glass in front of a clear fire, until the back of the glass feels hot, but not unbearably hot, when laid on the back of the hand. Gently brush off, with a broad camel's-hair brush, any particles of dust which may have settled on the film, and at once pour on the varnish, exactly in the same way as is done with collodion, returning the excess into the stock bottle. Move the plate backwards and forwards edgeways for a few seconds, taking care to keep the draining end lowermost. While the last drop is still hanging at the lower corner wipe it off with the finger or a piece of blotting-paper, and at once hold the plate again towards the fire, but not too near, because the vapour of the alcohol or other solvent of the varnish might ignite, and the flame leap to the surface of the plate and instantly destroy it, besides, probably, seriously burning the hand. The varnish should dry in a few seconds into a glassy surface. Should it dry *dead*, as it is called, or without gloss, either the varnish is bad, or the plate has not been sufficiently warmed. Waves or streaks on the film show that the varnish has not been properly applied, or that the plate has been too hot.

Varnished negatives should not be printed from till some hours after the varnish has been applied, because a slight *tackiness* will be apparent for some time, and this might cause the paper to adhere to the surface and pull off with it portions of the film.

STORING OF NEGATIVES.

The preceding instructions would be incomplete without some observations on the best methods of storing Negatives so as to prevent the film from cracking or peeling off by vicissitudes of temperature or moisture, or becoming scratched. For this purpose grooved plate boxes are generally used, the grooves serving to keep the plates apart. There can be little objection to this plan, provided the boxes are always kept in a dry room and at an equable temperature; and a great advantage in its favour is, that if each box is numbered and the contents tabulated, the operator can with little trouble lay his hand upon any Negative that may be wanted for printing.

When operations are carried on on a large scale it is usual to have a room fitted all round with grooved shelves, divided into compartments, each compartment being marked with a letter of the alphabet and each groove numbered. A catalogue of the Negatives, describing the subject, is kept in the room, and to each entry is attached an alphabetical letter and number corresponding to the position of every Negative. Thus it will be very easy to lay one's hand at any time on any particular Negative which may be required.

A series of cupboards running round the room, and fitted with grooved shelves in the same way, would be an advantage, because thus the Negatives would be protected from dust. In damp and cold weather a fire or stove in the room would be desirable. Indeed, as a general rule, the storing place should be kept at as equable a temperature as possible, and free from dampness.

Another plan of storing Negatives, which has much to recommend it, may be advantageously adopted by amateurs who only work occasionally. Pack up the Negatives by the dozen, or any other convenient number, the plates resting on one another, and having a piece of clean blotting-paper interposed between each to prevent scratching of the film. Tie the package tightly up in cartridge or brown paper, and attach to it a catalogue of the contents. Stow away in a dry cupboard.

CHAPTER XV.

PORTRAITURE.—POSITIVE AND NEGATIVE.

The Glass-house.—We commence this Chapter by remarking upon the advantages, or the contrary, to be expected from the use of a glass-house in Collodion Portraiture; adding at the same a few hints on the mode of its construction. Those who are accustomed to work beneath glass are often at fault on trying to take a picture in the open air, and obtain under such circumstances a hard and unpleasing portrait, with exaggerated contrast of light and shade. It is, without doubt, somewhat difficult to secure fine gradation of tone when the object is brilliantly illuminated, partly on account of the actinic power of the lenses which are employed in portraiture; and, therefore, unless the Chemicals are prepared purposely, the subdued light of a glass studio is likely to give the best effect.

Great diversity of opinion prevails as to the best mode of constructing a glass-house. There are, however, some principles generally agreed upon which may be here stated. The glass-house should, when practicable, have its greatest length in the direction of North and South, so that the sitter may be placed facing the North. It should be glazed with a pure colourless glass, as window-glass has usually a green tint, and when exposed for many months to the air becomes also more or less yellow, and absorbs the actinic rays. The glass should extend nearly to the ground. This is not so necessary for half-length portraits as for the *carte de visite* form, where equal illumination down the feet is required. A complete system of black-and-white curtains must be provided

both for the roof and sides, to throw the light on that side of the sitter which seems to be most desirable. The roof over the sitter and the sides, to the distance of about three feet from the background, must also be opaque, since a vertical light on the head is apt to solarize the hair, so as to make it appear grey, and will also give strong shadows underneath the eye. The end of the room where the Camera is placed had better be darkened, to prevent diffused light from falling on the lens, and also to relieve the eyes of the sitter from the painful expression often caused by too much light falling on the retinæ.

The background may be varied according to the taste of the operator, but to produce a neutral tint, the colour should be somewhat like that of common brown paper. Unless, however, the surface is quite dead, the effect of the background will depend upon the amount of light which shines upon it, so that it will produce a different colour in the open air from that given in the glass-house.

Proper ventilation is of the utmost importance, the heat being excessive in the summer months.

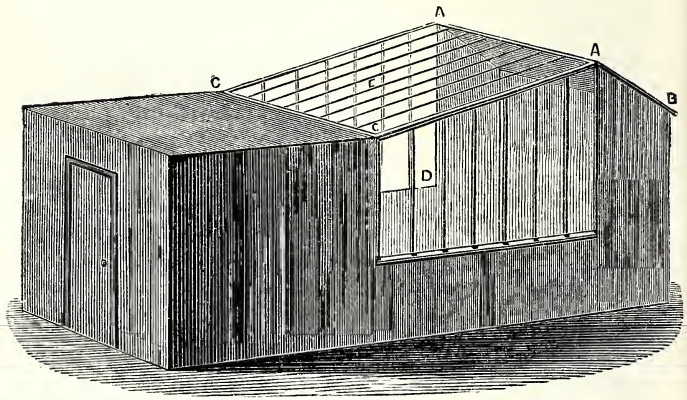
The developing room is frequently made smaller than is advisable, the consequence of which is, that it becomes almost unbearable in hot weather. It ought also to be more generally known that the vapour of Ether, when continually inhaled, has an extremely depressing effect upon the nervous system.

It may be observed that a horizontal light destroys the shadows entirely, and is suitable in the case of deep sunken features; but a light falling obliquely, partly from above and partly from the sides, and striking more upon one side of the face than the other, is the best in the majority of cases.

Some operators prefer to work in a ridge-roofed glass studio, regulating the light by means of a series of blinds. Others again select what is called the tunnel system, of which the accompanying illustration will serve to give some idea.

The tallest end of the background, B, is square—a great advantage in taking groups—while all the rest of the room not actually wanted for light may be built of any opaque material, to keep out the heat. The quantity of glass surface need bear very little proportion to the size of the room, as ten feet of glass from the sitter (or from A to C) is sufficient, no matter how long the room may be. If the room is sufficiently wide, there need be no side-lights at all. About three or four feet from the background of the under surface of glass, from A to B, may be blackened or built of

Fig. 11.



opaque material, as shown in the drawing. Supposing the room to be twelve feet wide, the highest part of the roof, A, should be about ten, sloping down for about eight or ten feet from the sitter, or A, to the lowest part, C, which may be a flat roof, leaded or tiled, or other opaque material, and which need be no higher than convenient to walk under. The sloping part just over the head of the sitter, A, B, may be hinged as a flap, to be lifted up when the weather will admit, as the warm air ascends to this, the highest part. This makes an admirable ventilator, even in this country,

in summer. The back, B, should be placed against a tall house, if possible, while the rest should be placed so as to have no obstructions. The interior of the room should be coloured a pale green colour, without pattern of any kind, as a pattern would distract the eye of the sitter.

The blinds on the top lights, E, may be made to pull down from A to C; spring blinds are best, if good. The side-lights, D, may be managed with curtains.

Many operators prefer to work in what is called a *ridge-roof* studio; but while the light is more difficult to control on account of the many fittings of blinds which will be required under different conditions of illumination, on the other hand the ridge-roof studio possesses some advantages.

Directions for Working in the Open Air.—When a glass-house is not at command, portraits may be taken in the open air. Indeed, a glass-house is only necessary as a protection from the wind, dust, and the inclemency of the weather. By selecting a proper situation, and by a judicious arrangement of screens, portraits with as much roundness and delicacy of detail can be taken out of doors as in. Mr. Shadbolt, who has given much attention to this subject, gives the following directions:—

"If we can find a spot where an angle is formed by two walls of a building—the walls standing respectively north-east and north-west—we have in fact nearly all we require; for by making a light wooden frame of about eight foot square, and covering it with stout unbleached calico-sheeting, we form a roof or canopy that can be readily fitted into the angle formed by the two walls, and that will give the requisite shade over the heads of our subjects. This square frame can also be readily raised or lowered at pleasure by a little ingenuity: and further, by poising our subjects so as to look towards either the north-west or north-east—that is, making each wall alternately the background—*either* side of our subject can be the most strongly illuminated, and the walls may either be painted of a suitable colour

for backgrounds, or covered temporarily with such materials as we may select for the purpose. The aspect indicated is not only preferable on account of uniformity of the light, but, as a rule, it will also be one most sheltered from wind in the summer time, when amateurs are most addicted to photographic pursuits.

"With regard to the point of holding the canopy in position, we have only to attach cords to each corner and gather them to a central point above it, so as to convert the frame into a kind of scale. To the point of convergence of the cords from the angles we attach a somewhat stouter single cord, and this, drawn through a small pulley, or even a ring, attached to the wall above will enable us readily to raise it. The cord can be run through a second ring or pulley, to enable us to draw it conveniently without interfering with the canopy itself; and the weight of the same may be counterpoised by a piece of iron, or even by a large stone. Lastly, a couple of long nails partly driven into the wall at the proper height may be so arranged as to prevent the frame from assuming other than a horizontal position. It is evident that with the aspect above indicated it will never happen that the sitter is exposed to the direct rays of the sun; but when from variation in the aspect this inconvenience does arise, it is so difficult a matter to apply an appropriate screen out of doors, that it will generally be better to modify the arrangement altogether."

When the desired conditions of a high building cannot be obtained, portraits may be taken in an open courtyard or garden by attending to the following precautions:—Always back up the sitter, if possible, by a dark ground, not less than seven feet square, to prevent diffused light from entering the lens. To make an effective screen, construct in the first instance a strong deal framework, consisting of a central portion with two lateral ones hinged to it. Cover the whole with oil-cloth, painted of a suitable colour, and as free from gloss as possible. By bringing one of the two sides forward, you are enabled to throw a shadow on

the face of the sitter, and by turning the other side back the whole arrangement may be fixed and rendered firm. Probably a screen will be required above to cut off the vertical light; and if so, the apparatus may be still further strengthened by constructing this part of a deal framework made to bolt down against the side which projects forward.

When everything is complete, stand in front of the lens and look in through the glasses from below upwards, to see if there be any reflection from the sky, or other bright objects. Unless the lens be placed very near indeed to the sitter, it is almost certain that there will be something of this kind, and if so a foggy picture will result. A large funnel of cardboard, lined with black velvet, should in such a case be carried out to a distance of about a foot in front of the lens, and the mouth of this funnel should be contracted as far as possible until it begins to cut off the corners of the field. This will render the image very clear, and will wonderfully improve the quality of the picture. Before exposing the plate, throw a black cloth over the end of the funnel, which will be found sufficient to exclude the light.

It is on account of the size of the glasses in a portrait combination, and the fact of their presenting so large a reflecting surface, that the above precautions are required. If small diaphragms were used, the sitter might be arranged with the open sky for a background without producing fogging.

It is beyond the scope of this manual to give instructions for *posing* and lighting the sitter, our main object being to describe the various Chemicals and apparatus, and to teach the student how to use them. They who desire valuable information on what may be called the Æsthetics of Photographic Portraiture, are referred to Lake Price's* valuable work, in which he treats of the composition of subjects with great clearness and artistic ability.

* "Manual of Photographic Manipulation." By Lake Price. J. & A. Churchill and Sons, New Burlington Street, London.

CHAPTER XVI.

PHOTOGRAPHIC ENLARGEMENTS.

SECTION I.

OPTICAL PRINCIPLES INVOLVED.

THERE are several processes by which enlargements are produced, but we shall here confine our attention to those that are employed commercially. The special merits or advantages of each method will be discovered in the course of our remarks. As important interests are connected with this department, we shall treat this subject with as much thoroughness as space will permit. Previous, however, to entering upon a detailed description, we must make a remark upon the optical principles involved in the production of enlargements, for when this is well understood the mere process by which they are to be made becomes more easily managed.

If any object—the figure of a man, for instance—standing at a certain distance in front of a Camera, say twenty feet, were photographed in the usual way, a Negative would be produced in the focus of the Lens, and if such Negative were replaced in the same Camera and taken into a darkened room, and arranged so as to have a strong light placed behind, and as to be received on a screen after being transmitted through the Negative and the Lens by which it was taken, a sharp image, of precisely the size of the original figure, would be seen projected on the screen, its distance from the Camera being equal to that at which the figure originally was. The Lens, therefore, has two foci—one before and the other behind. These are termed the "conjugate" foci. By altering in ever so slight a degree one of the objects at one focus, the other will also be altered. Let any object at a great distance be focussed sharply, such will be the solar focus; but if it then be made to approach, re-focussing will be necessary, for it will be found that in proportion as it approaches the Lens, so does the

focus recede from it. Hence is established the fact that each Lens has two foci, one situated at the image, and the other at the ground glass on which it is focussed. These two positions have a definite relation to each other, and hence they are called "conjugate foci."

It is easy to discover the second conjugate focus of any Lens, provided we know its equivalent focus, together with that of one conjugate. It is also easy to know both conjugates under all circumstances of variation of either of them from the lens; and consequently it is easy to tell the precise distance the negative and ground glass should be respectively from the lens, in order to produce an enlargement on any required scale of amplification—the practical outcome of the knowledge of the former.

Having ascertained by one or the other of the methods described in the Appendix the equivalent focus of the Lens by which the enlargements are to be made, the following rule determines the precise distance at which the Negative must be placed from the Lens on the one hand, and the distance that must intervene between the Lens and the focussing screen on the other. Having decided upon the number of times the enlargement has to be greater than the original negative, add 1 to that number, and multiply the sum by the focus of the Lens. This gives one of the distances. To find the other, divide the focus of the Lens by the times of enlargement required, and add it to the focus. The sum is the length sought for. The relative place of object and image depends upon whether the model is to be enlarged or reduced, for the rule applies to either case.

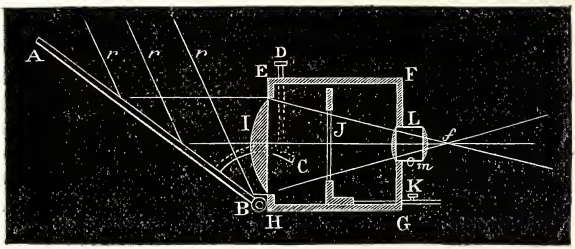
The advantage of a knowledge of this rule will be found when one is about to erect an enlarging camera for any special class of work, when by means of a simple calculation the Photographer can ascertain the precise length that a Camera has to be made to suit any requirement. Calculated upon the rules just given is a table for enlarging and reducing, given at the end of this book, which will save all trouble in estimating the relative positions of object and image in ordinary work.

SECTION II.

SOLAR CAMERA ENLARGEMENTS.

Enlarging by the Solar Camera, although extensively employed in America, is very little used in England. The form of Solar Camera most commonly preferred is that introduced by Woodward, which is shown in the adjoining diagram, in which solar rays, *r r*, fall

Fig. 12.



upon a mirror, A B, and are reflected upon the condenser, by which they are made to converge to a point *f*, passing through in their course, first, Negative J, and then the objective L. They are projected forward to a focus on a screen in front, on which is fastened by pins the sensitive paper. The wood-work of the Camera is represented by E F G H, and certain fittings by K D. The size of the condenser varies from nine to twenty inches; the larger the Lens is the more light it collects, and consequently the more quickly is the Positive printed. For instance, if a condenser of nine inches is employed, and with it an exposure of half an hour is required to obtain an enlargement by *direct* printing on silver-chlorized paper, a condenser of *double the area* will print the picture in half the time. The focal length of the condenser should not be less than twice its diameter, nor more than three times. If a small condenser is used, sufficient light may not

be collected to impress the image within a reasonable time. On the other hand, if a large condenser is used, the errors arising from spherical aberration become considerable.

The objective, or Lens L, may be an ordinary portrait combination; but care must be taken, in this case, that the Lens which faces the ground glass, as in ordinary work, now faces the Negative to be reproduced, J.

The Negative should be movable in the direction of the axis of the optical system by means of rack and pinion, so as to admit to any amount of enlargement that may be required.

An adjustable mirror, A B, is so placed and regulated as to throw the sun's rays through the Condenser, I, and the enlarging Lens, L.

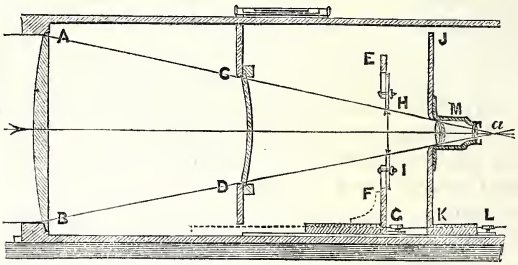
The management of the apparatus is very simple. It is sufficient to place the part E H B A of the Solar Camera in an opening in a darkened window, to communicate by means of the adjusting screws, B and D, the movements necessary for keeping the solar rays always reflected in the same direction, I *f*; to properly adjust the negative, J, so that its enlarged image is sharply formed on a screen, placed at a distance and perpendicular to the optical axis of the apparatus, and, lastly, to substitute for the screen a sheet of sensitive paper or other Photographic surface.

Considerable improvements have been made in the Solar Camera of Woodward, notably those by Dr. Monckhoven, who, to cure the evils arising from the aberrations of sphericity, whereby the various transmitted rays do not arrive at the same focal point, constructed his condenser on what is called the *dialytic principle*. This principle consists in intercepting the cone of rays from a single crown-glass condensing Lens, by a concave lens by which the aberrations both of sphericity and colour may be, the former considerably, and the latter altogether, remedied. The accompanying sectional diagram of this Camera will serve to show its construction.

The large condenser, A B, is what is called a *crossed lens*, one side being more convex than the other. The more convex side is placed towards the source of light. The refracted rays are intercepted in their passage through the Camera by the *correcting lens*, C D, which is concavo-convex, the concave side facing the condenser. This lens simply corrects for spherical and chromatic aberrations. The wooden frame, E F, which holds the Negative to be enlarged, is movable by means of a milled-head screw, G, nearer or farther away from the Lens, M, when required.

The front of the Camera to which the objective or enlarging Lens is fixed, is also movable towards or from the frame, E F, by means of the screw, L.

Fig. 13.



In other respects Dr. Monckhoven's solar apparatus is similar to Woodward's, and the mode of using them identically the same. At the same time, although both of them are called "Solar Cameras," they can be used for enlargements by artificial light. But in this latter case the enlarged image will have to be *developed* instead of being *directly* impressed, on account of the feeble actinism of artificial, compared with solar, light.

The printing by the Solar Camera has hitherto been usually effected upon plain salted paper and the printing, toning and fixing are conducted in a manner and to an extent similar to printing by means of the common printing frame.

When an enlargement is to be finished in colours in an expensive manner, it is now becoming more general to have it made on a more stable and permanent base than silver, hence carbon and platina printing find most favour for such a purpose. The details of these methods of printing will be found in another page.

In all cases in which the sun's rays are employed in connection with a system of lenses for enlarging, it is necessary either that a heliostat be made use of by which to ensure the sun's rays being constantly directed in one way only, or that the Camera itself be pointed straight at the sun, in which case the mirror is dispensed with. The Camera must be mounted on a strong axis inclined to suit the latitude of the place in which it is erected, hence when it is pointed upwards to suit the height of the sun at any one particular hour or season, it may by one progressive motion be kept directed to the source of light from morning till evening. If a toothed wheel be affixed to the axis of rotation, and geared into the one of the wheels of an ordinary clock, the Camera may be made to follow the direction of the sun with practical accuracy. This method of imparting motion applies equally to the mirror of a stationary enlarging Camera as to the case of a Camera mounted equatorially.

SECTION III.

THE COLLODION TRANSFER PROCESS.

This being the process by which almost all the cheap enlargements are produced, it is more employed than any other. The Camera by which this kind of enlarging is usually done is not a Camera at all in the usual acceptation of the term, but a simple framework for supporting the Negative, the Lens, and the glass on which the enlargement is made. The *Camera* proper is the apartment in which the operation is conducted.

Pointing upwards through a window so as to be

directed towards a part of the sky clear from any obstructions, such as chimneys or trees, is the base board of the structure, consisting of two parallel rigid boards made of pine. At its upper end is fixed a frame having a square aperture in it, and fitted with the requisite appliances for holding Negatives of the various sizes that are to be enlarged. A second frame, or, more correctly, a plain wooden board, holds the Lens, and to permit of focussing it is necessary that the mechanical arrangement be such as to permit this lens-holding frame to slide backwards and forwards upon the base-board. The ordinary focussing may be effected by the rack and pinion of the Lens, but the adjustment upon the base-board is necessary for rough adjustment. In routine work, such as the production of club pictures of a certain size, when once the general or rough focussing is determined, it will seldom have occasion to be disturbed, as the fine focussing can then be effected by the rack and pinion of the Lens. Towards the lower end of the base-board —which as constructed by many looks like a sort of tramway, the boards being twelve inches (more or less) apart—is erected a solid slab of wood not less in dimensions than those of the largest picture it is intended to make—14 by 17 inches for example. Near the bottom of this are two small projecting pins upon which to support the plate during exposure. The focussing screen consists of a plate of glass the dimensions of the plate upon which the transfer is to be made, and it is faced with white paper.

The Lens required is a small carte or quarter-plate combination, and its outer end, or that upon which is the wood, must be next to the focussing screen. No diaphragm is employed.

The Negative, one of *carte* size, having been placed in its holder, and the Lens adjusted, a large and sharp image will be seen projected on the surface of the focussing screen. By raising or lowering the Negative, the position of the enlarged image may be adjusted

with perfect accuracy upon the focussing screen. The distance between the Lens and this screen is determined by the rule already given, although in most cases the adjustments are effected by aid of a certain kind of intuition born of experience. The utmost care is required that *no light whatever* be admitted through the window into the room, but that which passes through the Lens. In saying this we except, of course, the special yellow light by which the development is effected. Failures in producing a high class of enlargement in which the whites are perfectly pure have frequently resulted from inattention to this requirement.

The Collodion for transfers may consist of any good Negative Collodion which has been prepared for several months—for the older it is, up to a certain stage, the cleaner will the enlargement be. But a good Negative Collodion is unsuited for transfer work until it has been diluted by the addition of from one-third to an equal part of plain uniodized Collodion. The object of this is to ensure a fine soft gradation of tints, from the highest light to the deepest shadow. The following is a formula by which several thousands of gallons of transfer Collodion have been made, and which, in the hands of intelligent manipulators, yields pictures of the highest excellence.

To twenty-five ounces of plain Collodion, containing about seven or eight grains of Pyroxyline per ounce, add a bromo-iodiser, composed of the following:—

Iodide of Cadmium	65 grains.
„ of Ammonium	25 „
Bromide of Cadmium	19 „
„ of Ammonium	11 „
Alcohol	5 ounces.

Provided a good sample of soluble cotton has been obtained, this forms a transfer Collodion which fulfils every requirement. It is desirable to add to it so much of an alcoholic solution of Iodine as to impart a deep sherry colour, although this is not required if

the Collodion be allowed to stand for a few months after mixing before being used. It is always desirable that transfer Collodion be made in large quantities, because by keeping for a few months, or even over a year, it acquires a charming ripeness that cannot be imparted by the admixture of Iodine or Bromine. Absolutely bare glass in the highest lights is an indispensable condition in Collodion transfers.

The Silver bath should not exceed twenty grains to the ounce.

The exposure must be determined by experience. If the Negative be placed so as to be backed by blue sky, the exposure will be longer than if white clouds formed its backing; and if Pyrogallic Acid be employed as a developer, the exposure will have to be much longer than in the case of Protosulphate of Iron. With the former, from five minutes upwards may have to be given; with the latter, from thirty to sixty seconds will suffice, unless the proportion of the restraining acid be increased to an unnecessary extent.

A good tone is obtained by the following developer:—

Pyrogallic Acid	100 grains.
Citric Acid	60 „
Acetic Acid	2 ounces.
Water	20 „

After this is applied, a short time will elapse ere the image appear, after which it will rapidly gain strength.

The mistake into which the inexperienced most usually fall, is to carry the development too far, by which a deep, heavy-looking smudgy picture results in the transfer, although when viewed as a transparency on the glass it may seem all right. Experience only can guide one in this matter, and fortunately it is an experience that may be gained in course of an hour's active work.

A twelve-grain solution of Protosulphate of Iron would develop the picture with a far greater degree of rapidity than the developer already given, and with an exposure very much shorter, but the tone would be

unpleasant. Citric Acid ensures dark tones, but to enable it to exercise this influence upon the image that is being formed, it is necessary that to counteract its retarding power, the strength of the iron be increased to a considerable extent, and also that the exposure be somewhat prolonged.

Cyanide of Potassium must not be had recourse to for fixing, on account of its tendency to give a light colour to the deposited Silver. The proper fixing agent is a saturated solution of Hyposulphite of Soda. But to recover an overdone picture, when it is inexpedient to make a second trial, Cyanide is very serviceable. It should be allowed to act upon the image until the high lights are seen to be denuded of the Silver by which they were obscured. Should the tone have been lightened to too great an extent by this treatment, it may be darkened by the application of a weak solution of the Chlorides of either Platinum, Gold, or Mercury. It is worthy of remark that a wash of the Mercury salt, when allowed to act no farther than to blacken the image, yields a picture which may be considered as tolerably permanent.

The image having been fixed and washed, a sheet of transfer paper, previously soaked in cold water for a few minutes until it has a slightly slimy feeling, is laid face down upon the Collodion picture, pressed into contact with it, and placed away to dry. After a few hours it may be raised at one corner and stripped away from the glass, carrying with it the Collodion picture. The "transfer" has now an exceedingly glossy surface, and when mounted on a card by means of thin glue, is ready for receiving oil colours without any preparation, should it be desired to finish it in that manner. If a mat surface be desired, the transfer should be stripped from the glass before it is quite dry.

The transfer paper for this process is made by placing four ounces of Gelatine in a quart of water, allowing it to soak for half an hour, and then placing the vessel containing it into warm water to liquefy the swollen Gelatine. Four grains of Chrome Alum, pre-

viously dissolved in a little warm water, are now added and incorporated with the Gelatine. Good stiff paper, similar to a fair sample of heavy writing-paper, having been previously cut into sheets the required size, is floated sheet by sheet on the surface of the Gelatine, which is kept warm by a water bath. Sponging over the paper with the Gelatine answers equally as well as floating it.

If the transfer does not strip away properly from the plate, it is caused by one or the other of the following :—The glass was dirty, and not sufficiently prepared with French Chalk, or the coating of the transfer paper with Gelatine has been too thin. In either case the remedy is obvious.

SECTION IV.

THE PHOTO-CRAYON PROCESS.

This process is closely allied to that just previously described, but it is simpler, and the results are more beautiful and artistic.

The image is produced in the same manner, but it must be made upon a large plate of glass, preferably the size of the frame in which it is eventually to be placed. It must also be vignetted: this is done by interposing a sheet of cardboard, having a suitable aperture, between the Lens and the Sensitive Plate. But, whereas in the Collodion Transfer process provision had to be made to allow the film to leave the glass, in this process it is necessary to cause it to adhere. This condition is secured by sponging diluted albumen—the white of one egg to a quart of water, over the surface, and allowing it to become dry before Collodionizing.

After the image is developed and fixed, either a warm or a grey tone may be imparted. But seeing that the picture is to be framed and present the appearance of a fine lithograph or crayon drawing, it is better to flow over the surface a weak solution of Chloride of Gold or Chloride of Platinum, by which both tone and

permanence are imparted. When dry the plate is varnished.

A toned sheet of drawing-paper, or white or tinted blotting-paper is now placed behind the enlarged transparency, special care being taken that it be in close contact with the film side. Upon looking at the picture through the glass it presents the appearance of being a fine drawing upon the paper; and this illusion is increased, and the pictorial merits of the picture enhanced, by previously producing upon the backing paper a few sketchy, crayon-like lines, so as to surround and merge into the vignetting of the bust. This must be done in a free manner with a soft black pencil or crayon. The appearance of the finished picture is such that even skilful artists, upon examination of fine examples, have imagined them to be carefully executed hand drawings, never suspecting their photographic origin, nor the extreme simplicity of the way by which the crayon effects were produced. Success depends upon placing the backing paper in close *mechanical contact* with the film. If it be not so the picture will have a hazy, out-of-focus appearance that is unpleasant. But optical contract between the backing and the image must also be avoided, else, for optical reasons, will the brilliant character of the picture be totally destroyed, and a dull image lacking all beauty be produced.

The rapidity with which photo-crayons may be executed, their permanence (apart from the circumstance of their being necessarily taken upon fragile material), their small cost, and their beauty, render this a process which, now that all patent restrictions have been removed, ought to be more generally known and practised than is the case at present.

SECTION V.

ENLARGING BY ARTIFICIAL LIGHT.

A magic lantern, having condensers of from four to

six inches diameter, furnishes the means by which enlargements may be produced by artificial light.

The source of light is of primary importance: when the extent to which the enlargement is to be carried is very great, the lime, magnesium, or electric light will be found indispensable; but if the extent of the amplification be only two diameters, then may an oil or common gas lamp be employed. The lime-light however is that form of illumination in which will be found the greatest advantage, especially if the oxygen be kept in a compressed state in a strong iron cylinder. In this way it is always ready for use, and the preparation for making even a single enlargement does not occupy more than a minute, while there is no deterioration of the oxygen such as takes place upon its being kept over two days in a rubber-lined bag.

The object-glass of the lantern must be an achromatic portrait combination by preference; for although any form of photographic objective may be made to answer, this fulfils better than any other the requirements of enlarging by artificial light. It is desirable that the lantern has a front capable of adjustment to such an extent as to allow of the lens being drawn out from the negative to an extent double that of its solar focus if desired; for this degree of extension is required to fulfil a condition sometimes demanded—viz., the reproduction of a picture barely larger than the original, or, in some instances, no larger at all. Lengthening tubes to effect the same end should be had when a lantern not originally constructed for enlarging is being used for this purpose. One such piece of tube, about two inches in length, and a second of four inches, will be found to answer every requirement, these being made so as to be used either singly or screwed one into the other.

When the enlarging is produced upon a surface of extreme sensitiveness, such as Gelatine emulsion, the amplification may be carried to a considerable extent by the common Gas-light or by the Petroleum lamp.

The modern lanterns in which the edges of two or more flames are presented to the condensers enable this kind of enlarging to be effected with satisfaction. The flat side of a flame may be likewise presented towards the condenser, but in this case it will be impossible to secure the highest degree of definition over the field of delineation, unless a diaphragm composed of a sheet of brass with a half-inch hole in it be placed immediately in front of the flame so as to limit its available size. For a similar reason all flames that are used in the production of enlargements ought to be as small as possible ; of course the greater their intensity the better.

SECTION VI.

CARBON ENLARGEMENTS.

There is no process of printing which lends itself to the production of valuable and really high-class enlargements as that by means of Carbon tissue.

The process itself is described at page 339, to which the reader is referred.

In applying to it the principle of enlarging, while it may be done with great success by means of the Solar Camera, it is found in practice to print them by the Direct Process from an enlarged Negative.

Negatives of this kind are made in the same manner by which an enlarged Positive is produced from a small Negative, only instead of its being the original small Negative which is enlarged, it is a transparency obtained from it by one or the other of the methods described in the Chapter devoted to Transparencies. The resulting enlargement, whether obtained by the ordinary wet Collodion or other process, is the Negative from which is printed the Carbon Positive.

Those who have seen the innumerable faded enlargements on Silver which have been produced in the Solar Camera, cannot but wish it were made compulsory on photographers to make all their enlargements by a permanent process such as Carbon.

CHAPTER XVII.

THE PRACTICAL DETAILS OF PHOTOGRAPHIC PRINTING.

SECTION I.

PRINTING ON PLAIN PAPER.

So far as the writer is aware there are at present in the market only two kinds of papers well adapted for this purpose—viz., Saxe and Rive, either of which may be adopted. In all cases there is a difference in smoothness between the two sides of the paper, and this is easily detected by holding the surface of each sheet in such a manner that a strong light falls on it at an acute angle. On the wrong side will be seen wire-gauze markings; or, in default of such being observed, the paper may be wetted at the corner, when one side will appear smoother than the other. The corner of the right side of the paper should be marked with a pencil to prevent future mistakes. This is not necessary when using albuminized paper, the right side of which is easily seen.

Salting the Plain Paper. Take of—

Chloride of Ammonium or Sodium	200 grains.
Citrate of Soda	20 ,,
Water	20 ounces.

Pour the solution into a flat glass bath, and immerse or float each sheet for about a minute. Hang them up to dry, by means of clips sold for the purpose, on a string stretched across the room. This operation need not be performed in the dark room. The *salted* paper will keep any length of time.

Sensitizing the Plain Salted Paper. Take of—

Nitrate of Silver	60 grains.
Distilled Water	1 ounce.

Prepare a sufficient quantity of this solution, and pour it out into a flat porcelain dish. Float the marked or smooth side of the paper on this for about a minute in hot weather and longer in cold. Pick up, by the corner, with a glass or wooden *clip*, and hang up in the *dark room* to dry spontaneously. It is then ready for use, but will remain clear and untarnished for twenty-four hours or more if the paper is of good quality. For further particulars see next Section.

Another method of Sensitizing is by means of Ammonio-nitrate of Silver, sixty grains to the ounce of distilled water, prepared thus:—Dissolve the Silver in one-half of the total quantity of water. Then take a strong solution of Ammonia and drop it in carefully, stirring meanwhile with a glass rod. A brown precipitate of Oxide of Silver first forms, but on the addition of more Ammonia it is redissolved. When the liquid appears to be clearing up, add the Ammonia very cautiously, so as not to have excess. In order still further to secure the absence of free Ammonia, a drop or two more of solution of Nitrate of Silver should be added, until a slight turbidity is again produced. Lastly, add the rest of the water.

To apply the Ammonio-nitrate Sensitizer, the paper should not be floated on it, because the solution soon gets quite black and the escape of Ammonia alters its character. Lay the sheet to be sensitized on blotting-paper, and apply the liquid evenly with a broad camel's-hair brush, kept for that purpose only, and carefully washed. Ammonio-nitrate sensitized paper requires no gold toning bath to get the print up to a bluish-black tone. In this respect it differs from all other printing sensitizers. The difficulty often is to get the print *warm* enough in tone to be pleasing.

The mode of conducting the printing, &c., will be described in the next Section.

SECTION II.

PRINTING ON ALBUMINIZED PAPER.

It is hardly worth one's while, now-a-days, to prepare his own Albuminized paper, seeing that there are difficulties attending its manufacture which require special care and special appliances. Moreover, as this is an article which does not deteriorate very readily, unless subjected to moisture, it can be kept safely in a place dry and free from dust; or, if it has to be sent to tropical or far distant countries, stored in soldered tins. In fact, the professional albuminizer can supply this article, anywhere, better and cheaper than one who only works occasionally can do for himself.

It is the custom at present with albuminizers to add very little salt to the Albumen—from five to eight grains; whereas, in former times, sometimes twenty or more grains were dissolved in each ounce of Albumen. This change is advantageous in several respects. It requires a weaker sensitizing bath, gives less violent contrasts of image, the paper keeps better after sensitizing, and altogether is better suited for the modern class of negative.

In cutting up the albuminized paper into sizes suitable for the bath, use a *paper-knife*, and do not touch the surface except with exceedingly dry and clean hands.

This precaution also applies more forcibly after the paper has been sensitized.

To render the Paper Sensitive.—This operation is, of course, conducted in the dark room; but it is by no means necessary that the room should be so dark as it must be when preparing sensitive films for development; inasmuch as in the former case printing is completed by the direct agency of light and not by a developer. Any darkening that would be hurtful to Silver-chlorized paper can therefore be detected by the eye. An amount of light short of this visible impression is permissible.

If the Albumen has not been salted at a higher rate than eight grains to the ounce, the strength of Nitrate solution given at p. 317 will be amply sufficient to sensitize it. Ammonio-nitrate of silver is not admissible, because Ammonia dissolves Albumen.

It is often difficult to avoid air-bubbles when sensitizing Albuminized paper, especially if the solution has been frequently used. The writer adopts the following plan, which, it is hoped, will be understood from a verbal description. The solution is poured into a clean glass or porcelain tray, after being filtered if necessary. The operator standing close to one end of the dish, takes a sheet of paper by two diagonal corners in both hands, lowers the end next to the body on the solution, and instantly with the hand thus set free seizes the upper corner and rolls, as it were, the sheet over the surface gently and evenly without allowing any Nitrate to get over the back of the paper. If the sheet is laid down rapidly, air-bubbles are sure to show themselves. They may easily be detected by examining the *back* of the paper after it has lain for about half a minute on the solution. There will appear a *puckering* up at those points, arising from the unequal expansion of the paper. To remove them, raise the sheet gently by one corner, and, with a twist of clean blotting-paper dipped in the solution, moisten the part; draw the bubble to the edge, or break it, and again lay down the paper.

If the room is warm, one minute's floating is enough; if cold, give two minutes or more. There is a disadvantage attending long contact with the Nitrate solution—viz., the printed picture will be too much in the *texture* of the paper instead of on the surface. This detracts much from its brilliancy. Besides, the pictures are more liable to fade, inasmuch as the silver having had time to penetrate, will come into contact with organic or other impurities which may exist in the texture. It is very difficult, if not impossible, to remove many of these afterwards by fixing and washing.

When the paper is hung up to dry there will still be considerable drainage from the lower corner. This should be collected and put into the jar for silver residues. After about two minutes' draining, a small piece of blotting-paper attached to the corner will absorb the rest. It will stick there until the Photographic paper is dry. These pieces should also be collected and preserved, because they contain an amount of silver well worth the trouble (see Appendix). The blotting-paper also serves another purpose, for, as the sensitizing paper curls up in drying, any surplus liquid at the corner will probably touch some part of the surface, and there give rise to a spot of extra sensitiveness.

It is better not to dry the paper artificially—that is, near a stove or fire—until the Nitrate from the surface has drained away. Even then, before printing, it should be placed for about a quarter of an hour in a position where it can imbibe the natural humidity of the atmosphere; else, when pressed in contact with the negative in the Printing frame, it will expand and give a blurred impression.

If the room in which the sensitized paper is drying be damp, the drying will proceed too slowly, and the Nitrate solution will go on penetrating deeper and deeper, thus producing an effect similar to prolonged flotation on the sensitizing bath.

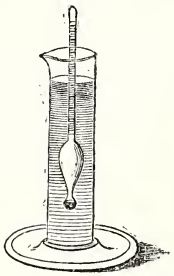
The principles to be kept in view when preparing Positive printing paper are these. The Albuminized paper should be bone dry, and floated for a minimum of time on a Nitrate solution strong enough to effect complete decomposition of the salts on the surface *only* of the paper. The drying should be *uniform* and rapid, in a room where there are no sulphurous or other silver-reducing fumes; and afterwards the paper, if not required for immediate use, stored sheet over sheet in a close portfolio also kept in a dry place. A good quality of paper thus stored will remain bright and clear for at least a week.

Moisture seems to be essential to the reduction of Silver-chlorized paper. Hence various devices have been devised for keeping it thoroughly desiccated in boxes containing quick-lime or other absorbents of moisture. These contrivances answer very well; but before laying the paper on the Negative it will be necessary to leave the former for a short time in the dark room exposed to the free action of air.

Care of the Sensitizing Solution.—The strength of the Nitrate bath decreases rapidly by frequent use, and hence an addition of Nitrate of Silver must occasionally be made.

The following convenient instrument (Fig 14) called a "Silver Meter," is now almost universally employed to ascertain the strength of Silver solutions. It is not quite accurate, but near enough for practical purposes. When greater accuracy is required, consult the sp. gr. table given in the Appendix.

Fig. 14.



It consists of a cylindrical vessel holding some three or four ounces, with an hydrometer of the common form. The Sensitizing Bath to be tested is poured into the glass, and the bulb floated in it, when the number of grains per ounce will be indicated by the part of the scale corresponding to the surface of the liquid. As these instruments are sold for a few shillings, and consequently are not made with much care, it is advisable to commence by preparing a 90-grain solution of pure Nitrate of Silver, to verify the correctness of the scale. Observe also that the indications of the hydrometer will cease to be trustworthy if the Bath contains Alcohol or Ether; hence an old Negative Bath, properly analysed, may be found to yield three or four grains of Nitrate per ounce over the quantity given by floating.

The solution of Nitrate of Silver becomes after a time discoloured by the Albumen, but may be used for

sensitizing until it is nearly black. The colour can be removed by Animal Charcoal, but a better plan is to use the "Kaolin," or pure white china clay. Shake up twenty ounces of Bath with a quarter of an ounce of finely pulverized Kaolin, and filter through paper. Kaolin often contains Carbonate of Lime, and effervesces with acids: if so, it must be purified by washing in dilute vinegar, or the Bath may become alkaline, and dissolve off the Albumen.

When Kaolin cannot be obtained, the Bath may be decolorized by shaking it up with recently precipitated Chloride of Silver in the curdy state. This substance has an affinity for the brown Sub-Albuminate of Silver which produces the colour, and gradually carries it down, leaving the supernatant liquid clear; but it is inferior to Kaolin as a decolorizer.

Old printing Nitrate Baths often become somewhat alkaline from the reaction of the Albumen; and the proportion of Silver falls so low that the coagulation of the Albumen is imperfect, and a white precipitate falls away into the Bath. In such a case, add to each ounce ten grains of Nitrate of Silver, and a drop or two of Glacial Acetic or Citric Acid.

PRINTING FROM THE NEGATIVE.

The Exposure to Light.—For this purpose reversing-frames are sold, which admit of being opened at the back, in order to examine the progress of the darkening by light, without producing any disturbance of position.

The shutter at the back is removed, and the Negative laid flat upon the glass, Collodion side uppermost. A sheet of sensitive paper is then placed upon the Negative, sensitive side downwards; next comes a layer of thick felt; and the whole is then tightly compressed by replacing and bolting down the shutter. The amount of pressure required is not very considerable, but if the springs of the frame become too weak after a

time, a few pieces of millboard may be placed beneath them.

This operation may be conducted in the dark room; but unless the light is very strong, such a precaution will be needless. The time of exposure to light varies much with the density of the Negative and the power of the actinic rays, as influenced by the season of the year and other obvious considerations. As a general rule, the best Negatives print rather slowly; whereas Negatives which have been under-exposed and under-developed, print quickly.

In the early spring or summer, when the light is powerful, about ten to fifteen minutes may be required; but from three-quarters of an hour to an hour and a half may be allowed in the winter months, even in the direct rays of the sun. It is always easy to judge of the length of time which will be sufficient, by exposing a small slip of the sensitive paper, unshielded, to the sun's rays, and observing how long it takes to reach the coppery stage of reduction. Whatever that time may be, nearly the same will be occupied in the printing, if the Negative be a good one.

In a dull light the writer has seen four days spent in getting one impression from a Negative; but pictures so obtained are not equal to others printed by a stronger light. The organic matter of the size reacts more or less upon the Nitrate of Silver, and causes yellowness of the whites of the paper; the toning process is also interfered with, as will presently be shown.

A light of excessive brilliancy is objectionable in printing, and especially so when the thermometer stands high. Complaints of unmanageable bronzing, with obliteration of details in the shadows, are frequent at such times, the reducing process being carried on with too much activity. Hence it is advisable, in the summer months at least, not to print by the direct rays of the sun. This point is further important, because the excessive heat of the sun's rays often cracks the glasses by unequal expansion, and glues the Negative

firmly down to the sensitive paper. An exception may be made in the case of Negatives of great intensity, which are printed most successfully upon a weakly sensitized paper exposed to the full rays of the sun; a feeble light not fully penetrating the dark parts.

When the darkening of the paper appears to have proceeded to a considerable extent, the frame is taken in and the picture examined. This, however, may be done in the open air, with care and expedition.

If the exposure to light has been correct, the print appears *slightly darker* than it is intended to remain. The Toning Bath dissolves away the lighter shades and reduces the intensity, for which allowance is made in the exposure to light. A little experience soon teaches the proper point; but much will depend upon the state of the Toning Bath, and albuminized paper will require to be printed somewhat more deeply than plain paper.

If, on removal from the printing-frame, a peculiar *spotted* appearance is seen, produced by unequal darkening of the Chloride of Silver, either the Nitrate Bath is too weak, the sheet removed from its surface too speedily, or the paper is of inferior quality.

On the other hand, if the general aspect of the print is a rich chocolate-brown in the case of Albumen, a dark slate-blue with Ammonio-Nitrate paper, or a reddish purple with paper prepared with Chloride and Citrate of Silver, the subsequent parts of the process will probably proceed well.

If, in the exposure to ordinary diffused daylight, the shadows of the proof become very decidedly *coppery* before the lights are sufficiently printed, the Negative is in fault. Ammonio-Nitrate paper highly salted is particularly liable to this excess of reduction, and especially so if the light is powerful.

The Toning of the Proof.—No injury results from postponing this part of the process for some hours, provided the print be kept in a dark place. But it is

not advisable to leave the print for a day or more before toning, since a chemical change may take place, the effect of which will be to interfere with the deposition of gold in the toning bath, and to destroy the purity of the whites.

The prints are first washed in a dish of common water, by immersing them one by one in a feeble light, but not necessarily in the dark room. After separating and turning them over two or three times, the water is poured off into the jar for preserving residues (see Appendix). More water is applied to them in the same way, and this also if very milky is consigned to the waste jar. A third portion of water will probably complete the washing. The symptom of removal of Nitrate of Silver is indicated by the hard water remaining clear. They are now ready for the toning bath, and their immersion therein should not be long delayed.

Formulæ for a Toning Bath.

We may premise that as the toning agent Chloride of Gold is usually sold in small hermetically sealed glass tubes containing stated quantities, and as a little of this very expensive salt goes a great way, the best mode of adding it to the bath is by measure, *not weight*. If the tube contains say thirty grains of Chloride of Gold, put it in the bottom of a clean and strong glass bottle. Break the tube by introducing a strong glass rod. Pour in fifteen ounces of distilled water, which will speedily dissolve the whole of the Chloride. *Each fluid ounce of this solution will therefore represent two grains of Chloride of Gold*, which should tone at least four hundred square inches of prints, or more than one full-sized sheet of *Saxe* or *Rive* paper. But in this respect a good deal depends on the nature of the paper, the strength of the sensitizing solution, the nature of the Negative, and the time that the paper has been kept after sensitizing.

Formula No. 1, *for two full-sized Sheets.*

Solution of Chloride of Gold	1 ounce or more.
Bicarbonate of Soda . . .	4 to 6 grains.
Clean Water	40 ounces.

This solution will not keep well, and should be mixed about an hour before use. After toning the prints, it should be thrown away.

Formula No. 2.

Solution of Chloride of Gold .	1 ounce or more.
Acetate or Phosphate of Soda	100 grains.
Clean Water	40 ounces.

This solution will not work well until several hours after mixing. Indeed, it may be prepared several days previously, and will work all the better for keeping. After the prints have been toned, the solution may be bottled up and kept for future use. No more Acetate or Phosphate will be required; but it will be necessary to add more gold solution immediately, or an hour or two, before use.

Various other salts to add to the Chloride of Gold have been worked into formulæ; but either of the above leavesnothing to be desired.

The prints are taken from the last washing water one by one and immersed in the toning solution in a flat bath. It is better not to put many in at one time. They are kept moving about so as to prevent unequal action. After a short time they will assume a bluish appearance; but that is not a true criterion of what their ultimate colour will be. If they are held up between the eye and the light some correct notion is gained; but neither is that a trustworthy guide, because some papers lose more of their tint in the fixing bath than others. The best plan is to try one, which is supposed fully toned, in the Hyposulphite bath, and note how it behaves. The tone will redden considerably in about a minute or less, but afterwards will regain part of the colour which it has lost. Experience is the

only guide in these matters. Generally it may be stated, prints on plain paper tone quicker than on an albuminized surface and lose less in the fixing bath.

The operator must be exceedingly careful not to allow a trace of the Hyposulphite solution to touch the toning bath, because this would infallibly produce prints covered with brown patches of Sulphide of Silver, which cannot be removed. A portion of the *toning* in the *fixing* bath does no harm farther than weakening the latter to that extent.

Toning should be conducted in a subdued white light, because in a yellow or monochromatic light it is impossible to judge of the depth of tone. The operator will notice that some prints from the same paper assume a rich colour more rapidly than others in the bath, while in some cases the best result that can be obtained is a feeble slaty blue. The tone depends a good deal on the quality of the Negative, all other circumstances being the same. Vigorous and clear Negatives give easily toned prints, and *vice versâ*. Temperature too affects the toning very considerably; hence it is recommended, in cold weather, to warm the solution, for, within certain limits, the sooner the required tint is got, the more brilliant are the prints.

Fixing the Proof.

The fixing bath is made in the following proportions:—

Hyposulphite of Soda	4 ounces.
Clean Water	1 pint.

This also is poured into a flat dish placed at some distance apart from the other, in case of splashes falling into the toning bath.

In conducting this double process it is well, when convenient, to have an assistant whose sole duty is to attend to the prints in the fixing solution, while the principal conducts the toning. The latter throws the print on the Hyposulphite solution while the assistant

instantly pushes it under, and so on until the whole have been immersed. But if an assistant is not at hand, one careful operator can do all the work. With one hand he moves about the prints in the toning bath, and as they get ready throws them one by one with that hand on to the fixing bath without touching it. The other hand instantly pushes them under.

While in the fixing bath the prints should be moved about to prevent them from sticking together and thus being irregularly acted on. In ten minutes the fixing will be complete; but as probably some of the proofs have been over-printed, pick out those which are too lightly or properly printed, and plunge them into a large basin or tub of clean water, leaving the others in the Hyposulphite until its solvent action on the image has reduced their intensity. Now an unpleasant difficulty occurs with prints immersed for a long time in Hyposulphite of Soda. The whites may become dingy yellow, and the half-tones suffer whilst the deepest shadows seem unaltered. This arises from the instability of Hyposulphites in the presence of acids of any kind.

Without entering into Chemical particulars, it will be sufficient to say that Hyposulphites generate their own acids when they act on certain salts of Silver, more particularly the Nitrate and Organic. The Chloride and other Silver Haloids are simply dissolved in this menstruum when neutral, without any acid being set free from the Hyposulphite. But as the Photographic print is not altogether made up of *pure* Chloride reduced by light, but is partly organic in its character, it follows that the Hyposulphite is decomposed when placed in contact with the latter, and Sulphur or Sulphide of Silver deposited.

The moral to be drawn from these facts is this: *Make the fixing bath decidedly alkaline by adding to it a little Carbonate of Soda, which will counteract the pernicious influence of the acid, and not interfere in any way with the dissolving powers of the Hyposulphite.*

It is a wise plan not to use a Hyposulphite bath for fixing more than one batch of prints, for as the salt is exceedingly unstable, it may after awhile contract acid from the air, not to mention that which itself generates by decomposition.

Washing the Prints after Fixing.

This is a tedious operation, for unless all the soluble Hyposulphite is removed from the paper, fading of the Photograph will quickly set in. Various forms of self-acting machines have been devised for this purpose; but although they save a great deal of labour, it is doubtful whether the best of them are so efficient as a systematic course of procedure by handwork in successive changes of water. If only about a dozen prints have to undergo washing, it may effectually be done in an hour by the following method. They are first soaked in five or six successive changes of water, draining them between each change. This will remove all the Hyposulphite from the exterior of the prints, but not from the interior. A print is now taken and laid on a sloping glass or slate slab. A soft sponge saturated with water is dabbed, but not rubbed, with pressure on the upper side, the print is taken up for an instant while the slab is flushed with water, it is again laid down on the other side, and the dabbing process repeated. When every print has gone through this operation they are hung up, or laid down on clean blotting-paper, to dry spontaneously, or they may be dried by the fire.

There is no more efficient mode of washing than the above, and when proofs are wanted in a hurry, it is invaluable, although entailing a great deal of labour.

Washing in Dishes.—When removed from the fixing bath the prints are thrown into a large dish containing clean water. The dish should be made of glass, porcelain, glazed earthenware, or slate. Wooden ones are sometimes used, and will answer very well if the pores of the wood are filled with varnish; if this

precaution be not taken, the Hyposulphite will soak into the pores and continue contaminating the water for a long time. *Zinc dishes must not be used,* as that metal will soon destroy a moist silver Photograph placed in contact with it, by reducing the metal which it contains.

More prints should not be thrown into the vessel than can be conveniently manipulated and separated within it, in abundance of water. The dish filled with water is placed in the sink near the tap. The prints as they come from the fixing bath are thrown in one by one and pushed under the water. They are then moved about gently, with the hand, for about a minute, so as not to tear them nor double them up. The proofs are now gently pressed down to the bottom with the outstretched palm of one hand, while the other gradually tilts up the vessel into a perpendicular position so as to discharge the water, the prints remaining on the bottom where they will stick for a minute to drain. More water is let in from the tap, taking care that it does not fall on the pictures, and the same process is repeated four or five times. All this can be done in about ten minutes. The prints are now allowed to soak for an hour or more; and the above process repeated three or four times, before setting them aside to dry.

It is a pernicious plan, although unfortunately one too often adopted, to place a large quantity of newly fixed prints in a dish and allow them to wash themselves by means of a small stream of water running in at one end and out at the other. The prints *will* stick together, and no amount of soaking can remove all the Hyposulphite from those in the interior of the batch, if this mode of washing is employed.

The drying should not be effected, as is sometimes done, by hanging the prints over strings stretched across the room, unless these strings have been previously cleansed from soluble and probably injurious matter by boiling in clean water. The writer adopts the plan of laying each print separately on a large

sloping board covered with two folds of clean *white* paper. Another plan is to pin each print up by one of the corners to a projecting shelf. This is good; but unfortunately some papers tear away by their own weight, allowing the print to fall on the ground. A third and perhaps the best plan, where space admits of its adoption, is to lay out the proofs on a sheet of clean linen or white calico stretched across the room.

Defects in Silver Positives on Paper.

1. *The Print Marbled and Streaky.*—These defects are often seen before the print is toned, if so, reject the prints. But more often they are only visible after the toning. *a.* The paper has been badly albuminized, the albumen having been allowed to drain off in streaks. *b.* The sensitizing solution sometimes flows off in the same way when the paper is hung up to dry, consequently the paper prints *deeper* where the current of silver has been running. It is easy to distinguish between these two causes of failure. In the first case the image is redder and fainter than the rest; in the second it is darker and deeper.

2. *The Prints clean on the surface, but, when held up and examined opposite a light, spotty.*—This disease is called *measles*, and is sure to destroy the Photograph after a very short time. The appearance presented is a series of irregular small yellow patches. These consist of that deadly enemy to all silver prints—viz., Sulphide of Silver, and lie in the *texture* of the paper. Their predisposing causes are a too weak fixing solution, too short immersion, but above all, a bad sample of paper.

3. *The Print has a Cold and Faded Appearance when Finished.*—*a.* The Nitrate of Silver has not been in sufficient excess in the paper. *b.* The Negative has not sufficient contrast; for it is impracticable to get a good print from a weak Negative. *c.* The print has been over-toned.

4. *Spots on the Surface.* — These, if white, arise

either from particles of dust on the Negative or surface of the paper; if black, from holes in the Negative. Other causes may also intervene, notably metallic particles in the paper. The latter can always be distinguished from all other spots. *There is a small black nucleus surrounded with a circle of white.*

5. *Yellowness of the High Lights.—a.* The paper has been kept too long after sensitizing. *b.* The fixing bath has been acid, or the action of a neutral one continued too long.

6. *Intense bronzing of the deep shadows* usually arises from having a large excess of silver in the sensitizing bath, and printing from an intense Negative which requires a long exposure to light.

7. *Yellow spots on the surface or back of a print* arise from the paper, before or after sensitizing, having come in contact with Hyposulphite of Soda. The least trace of the salt is sure to cause the mischief. If it has arisen from handling the paper with imperfectly washed hands, the impression of the fingers will be distinctly marked. Too great care cannot be exercised in handling or laying down Positive paper. Everything that touches it must be dry and clean.

8. *Mealiness of the prints* is a peculiar disease which may arise from several causes. The appearance which goes under this name is represented sometimes by exceedingly small red spots, and at other times by similar white ones. Of course, opaque particles of dust, either on the Negative or on the surface of the Sensitive paper will, to some extent, account for these. But this is not always the cause. The red specks most probably arise from the Albumen. The writer has never seen a specimen of these on plain salted paper.

9. *The Print refuses to tone.—a.* Often the fault of the paper. *b.* Long keeping of the print before toning. *c.* The toning bath has been kept too long and become inert. Add a little more solution of Chloride of Gold.

The above constitute the most important of the

failures in Photographic printing on paper by direct contact. Various others exist, but the causes of them are so very obvious, that any one can readily see their origin and apply the proper remedy after he has acquired a little experience.

SECTION III.

PLATINOTYPE PRINTING.

Whatever opinions may be entertained respecting the tendencies of silver prints to fade, it seems to be universally conceded that platinum pictures are durable. Not only are they permanent, but there is a peculiar charm about them which renders this style of printing exceptionally valuable for a large class of work. Those who have to expend much money in having photographs coloured may select the Platinotype in the full confidence that labour will not be thrown away, as is almost invariably the case when pigments are applied to silver prints.

The process about to be described was discovered by Mr. William Willis, Junior, who starting at first by assuming, correctly, that "platina black" was one of the most stable pigments known, next sought to discover by what means photographs could be printed in this substance.

Seeing that a solution of Ferrous Oxalate (Oxalate of Iron) in Potassic Oxalate (neutral Oxalate of Potash) was a perfect reducing agent of Platinum, he conceived the idea that as ferrous oxalate can be produced by the action of light on ferric oxalate, it ought to follow that if paper which has received a wash of chloride of platinum and ferric oxalate be exposed under a negative and then be subjected to a bath of oxalate of potash, the platinum will undergo reduction in proportion to the action of the light. When removed from the printing frame the pictures are feebly visible, owing to the reduction of the iron salt; for as yet the platinum salt, although in contact with the iron, has taken no part in the matter. The light has reduced the ferric into

the ferrous salt, and the latter is the reducer of the platinum. But as no chemical action can take place between two dry bodies of this nature, it is requisite that one of them be in solution. If the picture, as yet only very faintly visible, be immersed in a solution of potassic oxalate, the ferrous oxalate formed by the action of the light is immediately dissolved and exerts its reducing action upon the platinum salt lying in contiguity, which becomes of a rich black colour. It only remains to remove the remainder of the ferric oxalate by which the paper was sensitized, which is effected by a wash of oxalic acid, and the picture is finished.

Having given the foregoing outline of this interesting process, we are now in a position to enter a little deeper into details.

The paper is sensitized by spreading over it a mixture of potassic platinous chloride and ferric oxalate, made by dissolving 60 grains of the dry platinum salt in one ounce of the iron solution, or any smaller or larger quantity in the same proportions. This should be used as soon as mixed, as it keeps in good condition for a short time only, or from ten to twenty minutes, according to the heat of the weather.

Suppose it be wished to sensitize a surface of paper measuring $8'' \times 10''$, the simplest method is to place a piece of paper of sufficient size, with its prepared surface uppermost, upon an $8'' \times 10''$ glass plate, and then to fold the edges of the paper underneath the plate. By placing the plate upon a table (or, better, on a glass plate of larger size) the edges of the paper will be securely held between the plate and the table, and a smooth surface will be secured. The paper must be larger than the plate, to allow its edges to be turned over. Another method of securing a smooth surface is to place the paper on a glass plate of the same dimensions as the paper, and then to clip together the corners of the plate and the paper by means of American clips. Yet another method, which frequently answers well, is to pin the paper by its corners to the smooth surface

of a deal board. By the last two methods the corners of the paper are lost, which is not the case with the first method.

The sensitizer is now applied to the surface by means of a pad of cotton wool, or, better, by a pad made by enclosing a tuft of cotton wool in a small piece of flannel or old gauze underclothing.

To coat a surface measuring $8'' \times 10''$, from 25 to 30 minims of sensitizer will be required. This quantity should be measured and then poured on the middle of the sheet of paper, and immediately spread over the surface with a circular motion, in as even a manner as possible, by means of the above described pad. The rubbing should be very gentle, and should be continued until the coating becomes as uniform as possible.

The paper is then dried, and every means taken to keep it so. To this end it is stored in tubes containing a preparation of chloride of calcium and asbestos.

The printing is effected in exactly the same manner as ordinary albuminized paper, except that over the back of the paper a piece of thin vulcanized rubber must be placed. It is preferable, though not essential, that this sheet of rubber be somewhat larger than the negative, because then the edges of the sensitized paper are better protected from the action of the atmosphere. Probably in a dry climate, such as that of America, this and other precautions against damp would have less value than in England.

An important advantage in this process is the following: That although it is one entailing the operation of a so-called "development"—in truth, a *substitution* process—yet the undeveloped image is visible, and this to such an extent that not only is the proper time of exposure estimated by its appearance, but the important operations of "dodging" and "printing-in" are also easily carried out.

In practice the action of the light is on the ferric oxalate only, and the visible image is composed of ferrous oxalate, carbonic dioxide being given off, thus:

$$C6Fe_2O_{12} = 2C_2FeO_4 + 2CO_2.$$

Sometimes a blackening, or darkening, of the more solarized portions occurs. This is due to the presence of moisture in the air, which has found its way to the paper. On development no evil effect may be observable, but the darkening should be guarded against, as its presence shows that there has been "sailing rather too close to the wind." A darkening of the edges of the paper, where it covers that part of the negative corresponding to the rebate of the dark slide, may often be seen, especially when the rubber sheet does not lap over the edges of the negative.

As soon as the exposure of each print is complete, the print should be placed in a tin can or other suitable receptacle, containing a little dry chloride of calcium, to preserve it from moisture until it is developed, care being taken to avoid all possibility of contact between the paper and the chloride, which would produce white or yellowish-white spots on the print.

Development may be either proceeded with immediately after exposure, or, more conveniently, at the end of the day's printing. It must be conducted in a feeble white light.

The developer consists of 130 grains of Oxalate of Potash in each ounce of water, and as it keeps for an indefinite period, a large quantity of the solution may be made up.

The development is effected by floating the printed surface of the paper, for a few seconds, on this developing solution, which is conveniently contained in a flat-bottomed dish of enamelled iron or of porcelain, supported on an iron tripod. A Bunsen lamp, with rose-burner to spread the flame, forms the best means for supplying the heat; or a spirit lamp may be used. If a porcelain dish be used, care should be taken to prevent the flame from impinging directly upon it. A temperature varying between 170° and 180° Fahr. may be considered the standard temperature for the developer.

The bottom of the developing dish should be covered with the developing solution to the depth of at least one-fourth of an inch.

After the batch of prints has been developed, the solution should be put into a bottle for future use. Before again using this solution for developing it should be decanted from any green crystals (of no value) which may have formed, and then enough fresh Oxalate of Potash solution should be added to it to bring it up to its original bulk.

Large prints may be developed without any difficulty on a narrow dish or trough (having a length equal to the breadth of the print), by being slowly pulled over the solution contained therein.

In the foregoing operations various degrees of heat may be used, though a temperature at least as high as 170° Fahr, is generally advisable, and the exposures should be made to suit a hot development, as a rule. But when a print has been over-exposed, the only possible way to remedy it is to develop it on a cooler bath. Now on a cool bath the developing action is not so energetic as it is on a hot one, and the detail in the lighter portions is not so readily made visible. But more, the shadows also of the picture only slowly gain their full strength and richness; hence it may be laid down as a rule, that at *whatever temperature the development be conducted, the whole of the possible action must be permitted to take place*, that is, if *strong and homogeneous shadows* are required. The development, though completed in two or three seconds at a high temperature, may take half a minute or so at a temperature of 100° Fahr. This is a *very important point*, and not sufficiently appreciated, many appearing to suppose that when the whole of the *detail* is visible, no further action can follow.

The so-called "developer" of Potassic Oxalate is merely the vehicle or means of bringing the ferrous oxalate within chemical reach of the platinous salt; this it does by dissolving the ferrous oxalate, where-

upon the latter immediately reacts upon the platinous salt, producing metallic platinum and oxidation of the ferrous oxalate into ferric salts, thus:

$$3K_2PtCl_4 + 6C_2FeO_4 = Fe_2Cl_6 + 2C_6Fe_2O_{12} + 6KCl + 3Pt.$$

The ferric oxalate formed by ether with that from the parts not acted on by light, combines with potassic oxalate, forming the apple-green crystals of the double salt, potassic ferric oxalate, which crystallize out from a concentrated cold solution of potassic oxalate.

$$C_6Fe_2O_{12} + 3\,C_2K_2O_4 = 2C_6Fe'''K_3O_{12}.$$

The bath of Potassic Oxalate must never be allowed to become alkaline from any cause, a possible cause being over-heating of the dry oxalate on the sides of the dish, or elsewhere, by which means carbonic oxide is driven off and potassic carbonate results.

An alkaline bath will produce muddy prints; on the other hand, it should be only slightly acid: in fact, nearly as possible neutral; still alkalinity is far more to be feared than acidity.

It only remains to be said that the developed prints must be washed in *two* baths of a weak solution of Hydrochloric Acid to clear them. This solution is made by mixing one part of Hydrochloric Acid with 80 parts water.

As soon as the prints have been removed from the developing dish, they should be immersed face downwards in the first bath of this acid, in which they should remain ten minutes, or rather less; they should then be removed to the second bath, in which they should remain for a like period. While the prints remain in these acid baths they should be moved so that the solution has free access to their surfaces. The second bath should remain colourless; when it is in the slightest degree coloured it should be discarded, and a fresh one substituted.

On no account should the prints be placed in plain water on leaving the developer.

After the prints have passed through the two changes of acid, they should be rapidly rinsed, and then well washed in two or three changes of water during about half an hour. They are then finished.

The object of this washing in acid and water is to remove the iron salt with which the paper is sensitized.

These prints being on plain paper are better dried across glass rods or tubes. If wooden rods or strings are used for the purpose they should be kept very clean, otherwise stains are likely to occur.

SECTION IV.

CARBON, OR PIGMENT PRINTING.

One of the greatest drawbacks to Photography has been the great liability to fading of its products. Many and earnest have been the efforts to render silver Photographs permanent; but all of no avail, for by contact with air they must sooner or later fade away. Photographers have for a long time been painfully aware of this fact, hence the many attempts to rescue the Art from the stigma of evanescence. For this purpose Carbon or other suitable pigments are now to a considerable extent employed in printing.

It was discovered many years ago by Mr. Mungo Ponton, of Edinburgh, that certain organic substances, notably solution of Gelatine, when treated with a Chromic salt, such as Bichromate of Ammonia or Potash, spread over paper or other medium, dried and exposed to light, are no longer soluble in warm water. But to Mr. William Blair, of Perth, is due the discovery how to produce Carbon prints in half tone by development from the back of the Sensitive film. Light alone exercises no decomposing influence on these salts until they are brought in contact with the Organic body. The Chromic Acid is reduced to a lower Oxide of Chromium, and the liberated Oxygen unites with

the Gelatine which is oxidized into an insoluble resinous substance, or only soluble in proportion to the duration and force of the Actinic rays.

Preparation of the Pigmented Paper.—This can be best done by those who make a speciality of the manufacture and have abundance of space for drying the product uniformly. It may be stated generally, that the operation is conducted on the jack-towel system—that is, a long web of paper is fastened round two rollers placed at a distance apart. The lower roller is so arranged that the surface of the paper *just touches* a warm solution of pigmented gelatine in a trough. The pigment may consist of Carbon, either alone or with an admixture of Alizarine to produce the popular photographic colour; but pigments of any nature or colour may, if inert, be employed. A crank on one of the rollers is gently turned until the whole sheet has been covered on the outer side. The rollers are then raised or the trough lowered, whilst the crank is kept gently moving to enable the Gelatine to set uniformly. After this the web is cut and hung up to dry.

Sensitizing the Pigmented Paper.—It is of considerable importance not to use a strong solution of Bichromate for sensitizing, because, when the Gelatine is dry, crystals forming on the surface are apt to interfere with uniformity of printing, and make the tissue so sensitive as to be unmanageable.

Bichromate of Potash . . .	1 ounce
Water	1 pint
Liquor Ammoniæ	20 minims

During hot weather let the proportion of water be increased. A sufficient quantity is made to fill a flat dish to the depth of at least half an inch. The paper is cut into sizes rather smaller than the dish, which may be made of wood, porcelain, or zinc. A piece of paper is slipped, pigment side downwards, underneath the liquid, and instantly turned over, taking care to see that it is covered with the solution, and that there

are no air-bubbles on the surface. If any appear they must instantly be removed, either by a touch of the finger or a brush. The paper is almost certain at first to curl up above the solution, from unequal expansion; but this must be prevented by keeping it underneath, either by the hands or by means of brushes.

The temperature of the room in which the sensitizing operation is performed is of importance; for Gelatine, soluble in warm water, is more readily so in a heated place. Under ordinary circumstances, in this country, a temperature ranging not over 60° or 65° can be readily obtained. The pigmented paper, as usually prepared, will bear this degree of heat without the Gelatine slipping off, unless from prolonged immersion in the Bichromate bath. Should there be a tendency to solution of the Gelatine in hot weather, the plan of cooling the Bichromate solution with ice and immersing the paper for a minimum of time proves an antidote.

As a rule the paper is sufficiently sensitized when it becomes pliable. A longer immersion in the Bichromate bath does no harm farther than rendering the paper much more sensitive and consequently unmanageable. Remove superfluous moisture by the squeegee.

If the sensitized sheets are small, they may be hung up to dry in a dark room by an American or glass clip attached to a string stretched across the room. If they are 10 × 8 inches, or a little more, two clips will be necessary, one at each of the upper corners. If the sheets are still larger this is not a safe course of procedure, because their very weight would tear them away. Under such circumstances the suspension is best carried out in the following manner. A number of thin deal laths, about three quarters of an inch in width and sufficiently long to stretch more than across the whole breath of the sensitizing dish, should be provided. One of these is laid across the end of the bath, resting on the sides. As soon as the paper is sensitized, the corners nearest the lath are seized by

the forefinger and the thumb of each hand, and the end of the sheet placed upon the lath. The other lath is placed over this, and both gripped together with a couple of American clips. By these handles the sheet is raised gently from the bath and, after allowing the larger proportion of the liquid to drain off, is drawn over a glass rod. It is then suspended in a cool and dry dark room between horizontal bars on which the ends of the laths rest *edgeways* in grooves. After the paper has again drained for a short time, another lath is attached to the bottom by clips. The object of this is to prevent the sheet from curling up as it dries. Too slow drying conduces to insolubility of the gelatine; too rapid drying to its reticulation.

The same Bichromate bath may be used frequently, and apparently is not weakened; but it is gradually changed in some way which practically amounts to the same thing. And this is not to be wondered at when we bear in mind the singular reactions which take place when Chromic acid and some organic bodies are brought together.

When the Gelatine tissue has been sensitized, the sooner it is dried and used up the better. It should be printed on within twenty-four hours if possible; but if kept thoroughly dry, it will remain useful for several days, especially if a weak solution of Bichromate has been used for sensitizing.

Printing the Picture.—To those accustomed to silver printing, this will at first appear a difficult operation, but in reality it is not so after one has gained a little experience. The reason why it *appears* difficult is because no *visible* impression is made on the tissue. Various kinds of *Actinometers* or measures of Chemical light have been devised, none of which appears to the Writer to be so satisfactory and simple as a piece of silver-chlorized paper sensitized on a standard solution. The mode of using this Actinometer will be explained as we proceed.

The Negatives, after examination by transmitted

light, can be classified as a rule into four different degrees of printing density. On a corner of the glass is scratched with a diamond 1, 2, &c., as the case might be. The register will serve for future printings from the same Negative, but if a mistake in estimating the density has after trial been found to be committed, it can of course be easily remedied afterwards by altering the figure. After a little experience few mistakes will be committed in this respect.

Before printing on Gelatine from Negatives a precaution should be adopted, which is, however, not always necessary. A narrow strip of blackened paper is gummed all round the edges of the Negative; because it has been found that when light has acted strongly, the changed Gelatine will not adhere to the transfer paper with sufficient tenacity to resist the action of the warm water, which insinuates itself underneath and may destroy the picture. This bordering has been happily called the *safe edge*. An edging of black varnish answers equally well.

The plan which the Writer adopts for the exposure of the sensitive tissue is this. A dozen, say, ordinary printing frames are filled in the dark room. On each frame is a chalk mark representing the density of the negatives contained therein. All the frames are exposed to light, as near as may be simultaneously, and at the same time a bit of the silver-chlorized paper is subjected to the same actinic influence. When this paper registers, to the eye, a certain amount of darkening, all the frames marked 1 are turned over; when it registers a deeper colour the No. 2 set are similarly treated, and so on until the whole are supposed to be fully exposed. It may be stated, generally, that the time of exposure, with paper prepared as above directed, is about one-third of that required for printing from the same density of Negative on the most sensitive silver paper. Thus an operator who has been accustomed to the latter mode of procedure, may make an excellent Actinometer for his own guidance, by simply

exposing a piece of standard silvered paper under a negative in the printing frame, and judging, from an occasional examination of that, as to the time in which the Gelatine will be properly impressed.

Development of the Image.—In order to obtain a *non-reversed* print from an ordinary Negative, the exposed tissue must be attached to a temporary support during development. For this purpose a zinc, glass, or other plate slightly roughened may be employed, and, to prevent the image from adhering too closely, so that it cannot afterwards be removed, the surface of the plate should be smeared with a little wax and resin dissolved in turpentine. The excess of this is afterwards rubbed off with a clean rag. A quantity of these plates are prepared corresponding to the number of the prints to be operated on.

The next operation is to attach the exposed Gelatine to this support. Let us follow the progress of one example, which will explain all. The print is immersed in a tray containing cold and clean water. In a short time it has absorbed sufficient moisture to make it adhere firmly. When first immersed its tendency is to curl inwards. After a time it will become flat and then curl outwards. The time for removal is just before it becomes flat. The plate is now slipped under the water, the Gelatine side of the tissue pressed closely against it, and the whole drawn out in such a way as to avoid any possibility of intervening air-bubbles. Perfect adhesion is effected by expelling the superfluous moisture with a long slip of India-rubber inserted between two boards. This instrument is generally called a "squeegee," and is scraped with some pressure over the back of the attached print so as to expel as much water as thus can be driven out. After a few minutes, or longer, provided the tissue is not allowed to become dry, the development proper is commenced.

The plate, with the paper attached, is placed in a dish of warm water registered from 90° to 100° Fahr., and

remains there for a minute or two until the coloured coating begins to exude from the edges. Raise up gently one of the corners of the paper and it will leave the plate easily. Should it not do so, allow longer soaking; for if violence be used, in all probability the print will be destroyed. The paper when removed is worthless, and is thrown away; the greater part of the Gelatine has left it, and the picture, hidden amidst pigment, will be found attached to the zinc or other supporting medium. The plate is at once replaced in the warm water, when with gentle agitation, gradually the soluble Gelatine with its contained pigment is washed away and the picture appears. Now is the time to judge whether the exposure has been properly timed. If the image appears faint, the exposure has been too short. In this case there is no remedy. On the other hand if the details are too dark, hotter water will often clear them up. There is great room for judicious management in this respect. A final rinse in cold water removes any loose particles of pigment that may be lying on the surface, and sets the gelatine.

The next step is to transfer the developed print from its temporary support on to the final one. For this purpose "transfer paper" is required. Ordinary paper is too porous to admit of being used, but it is fitted for the purpose by being coated with a thin layer of Gelatine in which a little alum has been dissolved. The object of adding the alum is to convert the Gelatine when dry into a substance analogous to leather, and hence to render it insoluble in even very hot water. A piece of this paper, rather larger than the developed print is immersed in warm water for a minute or two until it feels slimy, and is then at once laid on the glass or other plate on which the image was developed, avoiding air bubbles. The "squeegee" is again applied to expel superfluous moisture and ensure close contact. When the paper is dry, *but not till then*, it is stripped from the plate, when it will be found that the picture

has left its first support and is imbedded as it were in the paper. Occasionally it may happen that the print even when dry exhibits a reluctance to leave the supporting plate. This arises from its having been imperfectly waxed. A gentle heat may be applied to the back of the plate.

Should any wax or resin be visible on the surface of the finished print, it may be rubbed off with a tuft of cotton wool impregnated with Benzol.

The above instructions refer to what is called the "double transfer" process, whereby the pictures are seen in their natural position, that is, *non-reversed*. But the impressed Gelatine tissue can at once be attached to its permanent support and developed thereon. This is called the "single transfer" method, which is much simpler in details, and would be universally adopted were it not that in printing from a Negative on glass the transferred image is *reversed*, that is, the right-hand side of the picture is placed to the left, and *vice versâ*, just as in a Daguerreotype or a Collodion positive on glass. To obviate this palpable drawback to an exceedingly simple mode of printing, the Collodion film may be removed from the glass and the negative preserved in a pellicular form, by which plan it can be printed from either side without any sensible loss of definition. One side would be placed in contact with Silver-chlorized paper, and the other with sensitized Gelatine as the case may be. Te remove the film from the glass, first dissolve off the varnish with alcohol, then apply gum water, followed when dry by an application of thick Collodion containing Castor oil. When dry the whole may be detatched as a pellicle. Immersion in water is sometimes necessary to aid in detaching it.

Photographing on Wood Blocks.—Carbon pictures may be made upon wood blocks for the use of the engraver. The block is smoothed in the usual way. A weak solution of Gelatine in warm water containing a little alum is made. The surface of the block, also warmed, is rubbed over with a little of this,

and all excess wiped away with a clean cloth. The exposed pigmented tissue, after lying for about a minute in cold water, is laid on the block, which is instantly pressed down on a smooth flat surface, such as glass, to expel air bubbles and secure perfect contact. The block is then set up edgeways for a short time, till the tissue is ready for development, which is effected in a manner not materially different from that already described. The block is held in the hand so that the surface and no more touches the warm water. After a little time the paper tissue is removed and the image developed by holding the block in the same way.

A few precautions are necessary. First, the pigmented tissue should be of that kind which has a minimum of Gelatine and a maximum of colouring matter. The object of this is to prevent the graving tool from *slipping* while drawing the fine lines. Second, immediately before developing, the *back* of the block should be moistened to prevent unequal expansion and probable cracking of the wood.

Photographs laid down in this way, so far as position is concerned, are exactly what the engraver requires—viz., a reversed image. But, on the other hand, he has no *lines* to guide him.

Carbon Transparencies.—Transparencies on glass, for use in the Stereoscope, the magic lantern, or for window decoration, may very easily be made by the Carbon process.

The printing must be carried a little deeper than is the case when paper is to be the final support; and such preparations as are made to facilitate the image being transferred from the glass to paper are here omitted, the most perfect adhesion being required.

The Carbon tissue, previously cut to the dimensions of the glass, is printed as previously directed, with a very narrow safe-edge: it is then "squeegeed" down on the glass and developed. The picture is then immersed for a few seconds in a saturated solution of alum, washed, and allowed to dry.

Solar Enlargements.—The Carbon process as applied to the production of enlargements of every kind is one of exceedingly great value. Its use with the Solar Camera has been much facilitated by the discovery that the insolubility started by the action of light may be continued in total darkness in presence of a slight degree of moisture in the atmosphere.

This discovery permits of a comparatively brief exposure being given in the Solar Camera, followed by the further development that goes on when the partially impressed tissue is suspended for a period of a few hours, or even days, in a dark cupboard. It is important to notice that this continuating action which goes on in the dark depends upon moisture, for in a dry atmosphere less progress will have been made after several weeks than will, when the atmosphere is moist, be made in a few hours. Those who desire to avail themselves of this property should have the moisture in their dark cupboards regulated by means of a hygrometer or a dry and wet bulb thermometer.

Further Applications.—Premising that the Carbon process is applied to opal glass, canvas, ivory, and, indeed, to every kind of surface, we must refer our readers for further details to the *Autotype Manual*, which is devoted to this subject.

SECTION V.

PHOTO-LITHOGRAPHY.

Many attempts have been made to render this process capable of reproducing Photographic half-tone, but all have been of no avail, or at the best have succeeded only very partially. The cause of failure lies in the fact that only *decided* lines will allow the greasy ink to *bite* or take hold of the stone.

Supposing that a map or any other outline, no matter how complex, has been drawn, and that it is deemed desirable to reproduce *fac-similes* or reduced copies by means of the Lithographic press, the picture is fastened

up flat and a Negative taken in the Camera by a non-distorting lens. The Negative must be clear and bright in the outline of shadow, and quite opaque in the parts represented by white in the original. Intensifying agents in the development are used for this latter purpose.

The following is Mr. Osborne's mode of procedure.

A sheet of plain positive Photographic paper is now coated on one side with a mixture consisting of Gelatine, softened and dissolved in water, to which a quantity of Bichromate of Potash and Albumen has been added. The paper, evenly covered with this fluid, is dried in the dark, when it will be found possessed of a smooth glassy surface, and a brilliant yellow colour. This surface is still further improved by passing it through the press in contact with a polished plate.

A suitable piece of positive Photo-lithographic paper thus manufactured is now to be exposed to the action of light under the Negative of the map already described. This is accomplished in an ordinary pressure-frame, the time required varying from ten to fifteen seconds to several minutes, according to the brightness of the weather; but it is always short compared with that necessary for the production of a picture on paper prepared with Chloride of Silver. The positive thus obtained presents itself to the eye as a brown drawing upon the clear yellow of the sheet. If the prepared surface of the paper were now moistened with water, and the attempt made to apply printing ink to it, we would find a strong tendency in the Albumino-gelatinous surface to behave towards greasy and watery substances in a manner quite analogous to that peculiar to a lithographic stone while printing. We would also find that the solvent action of water at any temperature is quite incapable of removing the picture which the sun has imprinted upon it. The light, in fact, has so acted upon the chemical substances brought together upon the surface of the paper that the organic matter is no longer soluble. These are the characteristics of

the change due to exposure which we have to remember.

But the exposed photographic copy of the original is not moistened, or subjected to any solvent action at this stage of the proceedings; it is, on the contrary, covered all over while dry with Lithographic transfer ink, which is accomplished by running it through the press with its face in contact with a stone which has already received a coating of such ink. After it is separated from the blackened stone it will be found to have brought away with it an evenly distributed film of inky matter, forced by the pressure into intimate contact with the unexposed as well as the exposed portions of the surface. This operation is known as "blacking" the Positive print. That now to be described is called "coagulation," its object being to effect a change of that nature upon the Albumen contained in the coating of organic matter. For this purpose moisture and heat are necessary, and both are applied very simply, by letting the blackened Photographic copy swim upon the surface of boiling water with its inky side upwards, for it is important not to wet that with hot water. After the lapse of a certain period, determined by the experience of the operator, he proceeds to the next step in the process, that of "washing off." For this purpose the print is laid upon a smooth surface, such as a plate of glass or porcelain, and friction with a wet sponge or other suitable material is applied to the black inky coating under which the Photographic image still exists, and to develop which is now the object in view. The operator soon becomes aware that the moisture which percolated through the paper from the back has exerted a softening influence upon the Gelatine in the sensitive coating, it has caused it to swell and to let go its hold upon the ink. But this change does not extend to those parts of the coating which were acted on by light; in other words, to those places which were unprotected by the opacity of the Negative; they remain intact, uninfluenced by the

solvent or moistening effect of the water. Accordingly, the operator finds a *fac-simile* of the original map gradually develop under his hand as he continues the friction. This process is proceeded with till all traces of ink are removed save those required to form the picture, which must be clear and distinct in all its details. Abundance of hot water is then poured over it, so as to remove every particle of soluble matter, and then it is finally dried, which completes its preparation. We are now possessed of a Photograph in Lithographic ink, identical in every respect with the original, not simply upon paper but upon Albuminized paper—a matter of much importance, as will presently be explained. The presence of the Albuminized layer under the picture is the result of the coagulation which took place while the print was swimming on the hot water; after that change no amount of washing could remove it, although the Gelatine was not proof against such treatment.

A stone to which a fine smooth surface has been imparted is now slightly warmed and put in the lithographic press. Upon this is placed inverted the Positive print, after it has been damped by lying between moist paper, and the whole is then passed repeatedly through the press. On examination the paper will now be found to have attached itself firmly to the stone, so that some force is required to separate the two. When the former is removed it brings with it the Albuminous coating, which gives to it while damp a parchment-like appearance. But the ink is gone; it has left the paper for the stone, and on the latter we find a reversed drawing of the map, one which, after it has been properly "prepared," will print as well as if it had been drawn by hand. The rationale of this method of transfer is easily understood: the greasy ink having a great affinity for the substance of the stone, combines with it to form a lithographic drawing in the strictest sense of the word, and while this is taking place the damp Albumen upon the paper holds the sheet

in its proper place, so as to prevent a shift of any kind, and enables the pressure to be applied as often as the operator wishes.

The stone is printed from in the usual lithographic way.

SECTION VI.

PHOTO-ZINCOGRAPHY.

This process in principle is the same as Photo-lithography, but some of the details are different. It was invented by Colonel Sir Henry James, and is now extensively employed in the Ordnance Survey Department at Southampton for copying maps, &c.

A suitable paper is floated for two or three minutes on a warm solution (about 100°) of the following substances:—Bichromate of potash, 2½ oz., dissolved in 10 oz. of hot water, to which are added 3 oz. of the purest gelatine previously dissolved in 40 oz. of hot water. The paper, after becoming dry, should be again floated on the same solution, and hung up to dry at the opposite corner to that by which it was first suspended in order to distribute the sensitizing solution uniformly. This must be done in the dark room. This paper will not keep long in a serviceable state even in the dark room, because the Bichromate gradually oxidizes gelatine without the action of light. Two days are about the limits of its keeping qualities.

The sensitive paper is exposed to the solar rays under a Negative in the pressure-frame as usual. One minute in bright sunlight is often sufficient. The general indications to judge of sufficient exposure, are the appearance of the parts where the light has acted most strongly. They should be of a deep tawny colour tinged with green, and the shadows yellow.

Now comes that part of the process where the lithographer steps in to complete the work of the photographer. The print is removed from the pressure-frame and *inked* by the following method:—

In an iron pot put 2 oz. of Burgundy pitch, 1 oz. of palm oil, and 1 oz. of bleached beeswax; place the pot over a fire, and as soon as they begin to melt, keep stirring the mass till they are thoroughly incorporated, which will not take place till the ingredients have nearly reached the point of ignition. Then remove the pot from the fire, and intimately mix with the contents 1 lb. of chalk, lithographic ink, and half a pint of what is called in the trade *middle linseed oil varnish*, both of which must have been previously thoroughly incorporated by pounding in a mortar.

When required for use, a portion of the ink is melted with sufficient turpentine to make it of the consistence of honey. A little is then placed on a printing roller, and a flat zinc plate inked with it in the usual manner. The print is then laid face downwards on the zinc, and the whole passed through a press, by which means it receives an even coating.

The print is then removed from the zinc plate, and laid back downwards on water at the temperature of about 100° Fahrenheit for a few minutes. It is next placed on a level slab, and all the superfluous ink removed with a soft sponge dipped in gum water. It is afterwards treated with repeated baths of warm water till the ground is quite clear. When dry, it is ready for transferring to zinc or stone.

Mode of Transfer, &c.—Colonel Sir Henry James's instructions on this part of the process are so very lucid and precise, that we cannot do better than quote them.

The Transference of the Print to Zinc, and Preparation for Printing.

When the zinc plates are received from the manufacturer, the surface has to be prepared to receive transfers. They are first planed with a razor blade, the back of which is set in a wooden handle, the ordinary edge is ground down flat so that there are two edges to scrape with in turn, like the edges of a skate. The

plate is thus cut down till all surface scratches, blisters, and other defects are obliterated.* It is then ground down to a flat surface with pumice stone, and smoothed with snake stone, to take out any scratches made by the pumice stone. Finally, a grained structure is given to it by rubbing with fine sand and water, and a zinc muller. The muller is simply a disc of zinc, about half an inch thick, and four inches in diameter, fixed to a wooden handle. It is grasped by the handle with the thumb uppermost, and rubbed over the surface of the plate with a circular movement.

The sand is brought to the requisite degree of fineness by sifting it through a wire sieve of from 80 to 120 holes to the square inch, according to the kind of grain required for the plate. The time required for two men to grain a zinc plate three feet long by two broad, has been found to be about an hour. As soon as this process is completed, the plate is thoroughly washed with water, and well dried. It should be kept from contact with any substance likely to communicate greasiness to it; and the sooner it is used for transferring the better, as the action of the atmosphere will tend to diminish the affinity of the surface for the greasy ink.

When it is desired to clean and prepare for receiving transfers a plate which has been used, the ink of the old transfer is cleared off with turpentine, the plate is then washed with strong alkali and cleaned with water, an acid is then poured over it. This is prepared by taking equal parts of Sulphuric and Hydrochloric acids, and to one part of the mixture adding twelve parts of water, and the plate is regrained in the manner already described.

The Photographic print is laid between sheets of damp paper for a few minutes, placed face downwards on the zinc plate, with two or three sheets of paper over it, and passed through the press.

If the transfer print is not more than three or four days old, it will be sufficient to pass it through once, but an old print on which the ink has had time to

harden, will require to pass through the press two or three times.

The sheets of paper covering the transfer are then removed, and it is damped with a wet sponge for two or three minutes; this causes the gelatine in the lines to swell, and makes the ink leave them more readily.

The print is then pulled carefully off the plate, and nearly the whole of the ink should remain on the zinc.

The transfer is now etched; the etching liquid consists of a decoction of galls and a little phosphoric acid, mixed with a thick solution of gum and water.

It is prepared as follows:—

Four ounces of Aleppo galls are bruised and steeped in three quarts of cold water for twenty-four hours; the water and galls are then placed in a vessel over the fire, and allowed to boil up. This decoction is then strained. The gum water should be about the consistence of cream.

One quart of the decoction of galls is added to three quarts of gum water, and to the mixture is added about three ounces of the solution of Phosphoric acid, which is prepared by placing sticks of Phosphorus in a pint bottle of water. This is stopped with a cork, in which is cut a small hole; the bottle is three-quarters filled with water, and the ends of the sticks of Phosphorus rise above the surface and become oxidized by the air admitted into the bottle.

The Phosphoric acid, as fast as it is formed, is dissolved by water. In a few days the solution is strong enough for use.

The etching liquid is poured on the plate, and wiped over the surface with a sponge or camel's-hair brush. It is allowed to remain on for a short time, varying with the strength of the design. With fine work twenty seconds would be sufficient. Strong lines will bear the action a minute without injury. As soon as the solution has acted sufficiently, it is wiped with a soft cloth dipped in water, care being taken to remove all trace of it if there are fine lines.

The transfer ink is next cleared from the zinc plate with turpentine, or, if the design is weak, with turpentine mixed with olive oil and gum water. It is then rolled up with printing ink, the roller being very thinly and evenly coated. Impressions can then be printed in the usual manner; 1,500 is not an unusual number for the plate to stand without sensible deterioration.

The photographic print can be transferred to a lithographic stone in a similar manner.

When the subject admits of it, paper enamelled with zinc white should be used, as the impressions produced are most perfect.

It is prepared in the following manner:—

Four ounces of Russian glue are soaked in three quarts of water for some hours, and then heated till dissolved; a pound and a half of zinc white is ground with water on a slab, and then mixed gradually with the solution of glue and passed through a hair sieve.

A coating is brushed on the paper with a *pound* brush, and the streaks are obliterated by going lightly over the surface with a flat camel's-hair brush. A second coating is applied in a similar manner, and hung up to dry. When dry it is ready for use.

SECTION VII.

WOODBURY'S PROCESS; OR, PHOTO-RELIEF PRINTING.

Any good Negative suits for this process, but the details of manipulation are not very easy.

First Stage: Preparing the Tissue.—A clean glass plate is smeared over with beeswax, which is then rubbed with a clean cloth till the coating is infinitesimally thin. A strong-bodied and tough Collodion is poured over the waxed side of the glass in the usual way, and allowed to dry. The plate is coated on the Collodion side with a thick and warm aqueous solution of Gelatine, containing from fifteen to thirty per cent. of Bichromate of Ammonia or Potash, and is then laid on a levelling stand, in the dark room, to set in a uni-

form sheet. When the film has set, the plate is put into a closed drying box containing fused Chloride of Calcium, which soon desiccates the gelatine by absorbing the moisture. The compound film of Collodion and Gelatine can now be raised from the glass in one unbroken sheet by cutting round its edges with a sharp knife and gently raising it up. With as little delay as possible the tissue is subjected to the next operation.

Second Stage : Impressing the Tissue.—The Collodion side of the tissue is placed in contact with a Negative in a common printing frame, and subjected to the *direct* solar rays, which should fall perpendicular to the surface of the glass, otherwise the image will lose much of its sharpness, for the following reason :—As the actinic impression has to be made through an appreciable thickness of insensitive Collodion intervening between the surface of the Negative and the sensitive Gelatine, and has also to penetrate through the latter to some considerable depth, any parallax or change of relative positions of the different parts of the Negative, arising from various obliquities of the light, would seriously affect sharpness of definition, and, to some extent, truthfulness of delineation. The above remarks will be appreciated by those who, by inadvertence, have made a print from the wrong side of a Negative on glass. The image is all confused. But if any one tries the experiment of printing from the wrong side of a Negative on very thin glass, by placing and keeping it quite perpendicular to the sun's rays, at the same time excluding, as far as possible, all diffused light, he will find his print nearly, if not quite, as fine as if the sensitive paper had been in immediate contact with the Negative image itself.

The above are the principles which must be attended to in impressing the sensitive gelatine film. Artificial light from the charcoal points of a powerful magnetic battery may be used ; but in this case, as the printing frame must be placed near the source of light, there will be considerable parallax.

Third Stage: Making the Mould.—When the exposure is completed, the unimpressed Gelatine is washed away. To do this, the Collodion side of the tissue is pasted down flatly with a Benzolic solution of India-rubber on a piece of clean glass, and the edges varnished. The whole is placed in a dish of warm water, which dissolves off all the gelatine where light has not acted, and the rest exactly in proportion to the actinic impression, leaving a *depressed surface* in the high lights corresponding to the densest portions of the Negative, and a gradually increasing *relief* through all intermediate tones up to the deepest shadows. The film still attached to the glass is dried, and can then be easily detached in one unbroken sheet by cutting round the edges and gently raising it.

At this stage the value of a little Prussian blue, mixed with the Bichromated gelatine, is obvious. Pure gelatine, when in thin stratum, is transparent, and the inequalities on the raised surface corresponding to the lights and shades of the Negative could hardly be appreciated without some pigment being mixed with the Gelatine. Prussian blue is the best to use, because it offers little obstruction to the Chemical rays during exposure.

The mould is now complete.

Fourth Stage: Making the Printing Die.—For this purpose a composition of lead and type metal is used. On a block of this composite metal, about a quarter of an inch thick, the Collodio-gelatine mould is laid, gelatine side downwards, placed in a hydraulic press, and subjected for a few minutes to a pressure of over a hundred tons. The result is a sharply defined and reversed-relievo image on the metallic surface. The high lights are, of course, now raised and the shadows depressed. Strange as it may appear, the gelatine mould, although thus squeezed with such enormous pressure against a metallic body apparently harder than itself, has not suffered in the least, and may be used for taking many similar impressions, all as sharp as the first one.

The metallic die is now trimmed to the size of picture

required and bevelled on the upper edges, when it is ready for casting out the *bas-relievo* proofs on glass, paper, or other suitable medium.

Fifth Stage: Casting or Printing from the Die.—To get proofs on glass and other rigid media, the die is placed on a level slab and rubbed over with a little oil. A small pool of aqueous solution of gelatine, impregnated with Carbon or any desired pigment, kept ready at hand in a warming apparatus, is poured on the middle of the die. Immediately the glass or other plate, also warm, is pressed thereon with the hand for an instant, and left in position till the gelatine sets, which might be in about two or three minutes. After that, the glass or other medium, with the picture firmly attached to it, may be removed, and the superfluous pigment round the edges scraped off. The whole is then varnished. As one man can work several dies, and as the die requires oiling only once for five or six impressions, the prints can be turned out at the rate of about one per minute.

When paper or other flexible porous medium is used to receive the picture, the process of printing is slightly different. The paper must first be impregnated with some substance which renders it *non-absorbent*, else some of the pigment would be squeezed into the pores of the paper instead of being pressed away from the parts of the die in highest relief. A pressure frame is also required to press the pliant medium in close contact with the pigmented die.

The rationale of the final *casting* on glass, paper, &c., of this ingenious process, is very easily understood. The die, or metallic impression from the gelatine mould, is something analogous to a Queen's head on a coin, but not in such high relief. The most elevated portions of the die corresponding to the high lights of the picture squeeze away the *whole* of the pigment, and those less elevated press it out in proportion to their greater or less elevation. Thus perfect gradation of tone is secured.

Two or three drawbacks to the extensive use of this process exist. First, the die cannot be printed from along with letter-press. Second, no means have been devised whereby the crushed out pigment should not smear the borders of the paper, &c., on which the picture is impressed. And third, the production of large images seems to be an impracticable operation.

SECTION VIII.

THE STANNOTYPE.

The Stannotype is closely related to the former process, and, like it, is the invention of Mr. Woodbury. Its distinguishing feature consists in the method by which the printing surface is made.

A transparency obtained by any suitable process is used as a *cliché* to impress an image on a sheet of Carbon tissue which contains a large proportion of gelatine and but little colouring matter. This is sensitized by immersion for five minutes in a six per cent. solution of Bichromate of Potash. It is then dried quickly over Chloride of Calcium or Lime, and then exposed to light in the printing frame under the transparency, a "safe edge," as described in the Chapter on Pigment Printing, being employed. The image is developed upon patent plate-glass, half an inch larger each way than the opening in the mask, and the temperature of the water employed in developing should not exceed 110° Fahr.

After becoming dry, which is hastened by first placing the plate in Alcohol for some time, it will be seen that there is a great degree of relief in the picture, which is now intaglio. It is then covered with a sheet of tinfoil, either plain or coated with a delicate steel layer, and to ensure adhesion it is previously coated with a thin solution of india-rubber in benzole. By passing the glass plate thus prepared between a pair of india-rubber rollers, with proper

precautions not to fracture the glass, and yet to have sufficient pressure applied to bring the tinfoil into contact with every part—even the deepest indentations of the intaglio—a surface is obtained from which impressions may be obtained in the manner described in the previous Chapter.

SECTION IX.

PHOTO-BLOCK PRINTING.

Among various ways of producing surface-printing blocks by means of Photography, there are two which are much employed.

(*a*) *Gelatine Reliefs.*—A plate of glass is coated with Bichromatized Gelatine and dried. It is then exposed under a Negative of any line subject, such as printed matter or engravings, and transferred to a dish of cold water. The parts unacted upon by light immediately swell and stand in relief, leaving the printed matter flat as before.

From this relief a cast is obtained by an electro-metallurgic process, by plaster of Paris, or by one or another of the various methods so well known in connection with stereotyping processes.

(*b*) *Line-etched Reliefs.*—Paper having been sized with Albumen and Bichromate of Potash, and carefully dried in the dark, is exposed in a printing frame under the Negative. It is then blackened all over with lithographic transfer ink, and laid face upward in a flat dish of cold water. By applying gentle friction to the surface the whole of the ink is removed, with the exception of that which adheres to the printed matter.

The transfer is next laid face down upon a smooth and clean zinc plate, and passed through a press, by which the ink is set off on the plate. The image is then rolled up and strengthened in the manner practised by lithographers, an application of powdered resin and bitumen made to strengthen its acid-resisting proper-

ties, and after a gentle heat to fuse the resin, the plate is placed in a vessel containing greatly diluted Sulphuric Oxhydrochloric Acid, by which the unprotected parts of the plate, representing the whites, are dissolved away, leaving the other parts standing in relief. Undercutting of the lines by means of the acid is provided against by alternating the etching process with occasional applications of the printing roller, followed by the dusting on of resin and fusing. The fine powder applied diagonally by means of a flat camel's-hair brush, followed by fusion, answers a similar purpose—viz., the protection of the sides of the raised lines from the undermining action of the acid.

There are other Photo-etching processes, some of them based upon the sensitiveness to light of Bitumen, and its becoming insoluble by exposure, and consequently forming an etching ground; others by a similar property residing in Bichromatized Gelatine, the non-exposed parts of which are permeable by solutions of Perchloride of Iron, or Chloride of Platinum, while the exposed portions are acid-resisting, but the processes we have described are those most approved in practice.

SECTION X.

COLLOTYPE PRINTING.

The method of printing from a film of Gelatine by means of printers' ink, has received various trade designations, such as Lichtdruck, Heliotype process, &c.

The principle on which the process is based is analogous to that of Photo-lithography, with this important difference—viz., that in Collotype printing the sensitized Gelatine is so changed by the action of Light that it takes the printers' ink exactly in proportion to the actinic impression made.

Mr. Sawyer, who has been eminently successful in this mode of printing, furnishes the following details of manipulation :—

A mixture is made of Gelatine, Albumen, and Bichromate of Potash, the ingredients being well beaten together; when the froth has settled down the mixture is filtered. The plate, having been previously levelled in a drying box, and warmed up to a temperature of 100°, is coated with a portion of the preparation, which is made to flow all over the plate and a portion over each edge; the plate is restored to its drying-box, and in about two hours or so the first coating is dry. The second preparation is composed of Gelatine, one to six, and a small portion of albumen, and sensitized with a Bichromate. When these are thoroughly dissolved they are whisked well together, and whilst being agitated a small quantity of an alcoholic solution of resinous gum is added; an emulsion is instantly formed, the particles of the gum being entangled with the gelatine. There is added a trace of Nitrate of Silver, with a small quantity of a solution containing an alkaline iodide. The whole, after being well stirred together, is filtered; the plate is again levelled in its drying-box. When all is ready the plate is placed in a porcelain dish of warm water, the excess of Bichromate of the first coating is washed away, the heat of the water and the residue of the chemicals remaining coagulate the albumen, and produce a very delicate, slightly-porous surface admirably fitted for the reception of the second preparation, which is poured on the plate whilst still moist. Care is taken to let it drive off the superfluous water, and a portion of the preparation itself is allowed to escape over each edge, which has the effect of binding down the film firmly to the glass. The plate is restored to its drying-box, and at a temperature of 90° or 100° becomes dry and ready for use in two or three hours. When dry and cool a Negative is laid down upon the plate-glass of the pressure-frame, and the plate-glass bearing the sensitive surface laid upon it. The progress of the printing can be easily ascertained by looking through the plate from the back. When the picture appears well, and all the detail visible, it is done

enough. After exposure the plates are washed with cold water, rinsed thoroughly, and allowed to dry spontaneously; they are then ready for the press. Plates prepared by this method have exceedingly thin films, not exceeding the thickness of writing-paper, and to this fact perhaps is due the exquisite reproduction of fine and delicate detail. In thick films there is an appreciable and, very frequently, a strong relief, requiring enormous pressure to force the paper into it; in these thin films the process is exactly analogous to that of lithography, and the pressure required is comparatively trifling.

The plate, when dry, is levelled on the bed of an ordinary lithographic press. A little plaster of Paris is run on a lithographic stone, and the glass plate is laid upon it whilst it is still fluid. No plate laid down in this way will ever break, whatever pressure may be applied to it. This plan, however, being rather troublesome, the following is usually adopted:—Venice turpentine thickened with a little wax is smeared on a slab or lithographic stone, and the plate is worked down upon it for a few seconds; it soon becomes set, and may be printed from without the slightest risk—only beware of any grit between the glass and the stone. Having, in one or other of these ways, got the plate upon the bed of the press, it is carefully levelled up, and well sponged with cold water, dried off with blotting paper, then wiped with a piece of fine soft muslin, and ink rolled into it with a lithographer's leather roller. If the plate is over-exposed, or under-exposed, a judicious use of thicker or thinner ink will still produce good results. Sometimes two or more inks of the same or varying degrees of stiffness are used in colour-printing, frequently only one. The operation of printing is one requiring delicacy, taste, and skill in the rolling; and the reason that the productions of Berlin and Munich are so exquisite is that they are able to command the very finest trained skill in lithographic printing.

CHAPTER XVIII.

THE GELATINE EMULSION PROCESS.

In 1871 was initiated what has proved to be a revolutionary power in the production of dry plates possessing a degree of sensitiveness never previously obtained by any process wet or dry. In that year Dr. R. L. Maddox submitted to the editor of one of the London weekly photographic journals several negatives he had taken by an emulsion of Bromide of Silver with Gelatine, instead of Collodion, which had hitherto been employed. Having to retire for a time from the experimental practice of photography, he published the details of his method of proceeding in order that others might continue the investigation. This has been done, with effects of a scientific, artistic, and commercial nature which are truly astonishing. The wet Collodion process has now been banished from a large number of operating rooms; for among other properties inherent in dry Gelatine plates is the desirable one of a degree of sensitiveness far exceeding that of Collodion. This, in addition to the convenience arising from having in readiness for use at all times a supply of dry plates, which being supplied through commercial sources in every size, of extreme sensitiveness and that excellence arising from competitive specialité manufacture, now enable the photographer to economize his labour, dismiss his sitters quickly, and, above all, to secure effects in expression hitherto obtained with difficulty on account of the longer exposure required. As regards the pictorial effect capable of being obtained out of doors, the editor of this manual has obtained, from the deck of a steamer swiftly moving in one direction,

sharply defined and fully exposed negatives of steamers, yachts, and other ships, rapidly proceeding in an opposite direction. This exalted sensitiveness in dry plates is owing to the substitution of Gelatine for Collodion as the agent for presenting the sensitive Bromide of Silver in a pellicular form.

While it is not necessary that any detailed account of the Gelatine emulsion process from its first publication by Dr. Maddox up to the present time be given, yet a few remarks of a somewhat historical nature will conduce to the better understanding of the advances that have been made.

As first presented to the public, the Gelatine emulsion process was slow, in the sense of requiring a long exposure in the camera; but after two years others entered the field of investigation, and succeeded in obtaining a degree of sensitiveness at first equal to, and subsequently exceeding, wet Collodion. The method by which this sensitiveness was obtained was kept a secret. So possessed had the photographic mind been with the idea of the impossibility of any dry plate being more sensitive than the standard wet Collodion, that one professional manufacturer of Gelatine plates (Mr. R. Kennett) was compelled to issue them of a lower degree of sensitiveness than he had at first manufactured, simply because photographers, not realizing the possibility of such great sensitiveness, spoiled many plates from over-exposing. It was only after the publication of an article by Mr. Charles Bennett, descriptive of his method of preparing the emulsion, by which he had secured certain exceedingly rapid effects not previously deemed possible, that public attention became awakened to the great value of the new process for securing, in a manner more thoroughly than was previously possible, complete delineations of life and character.

The discovery, although important, was in itself characterized by great simplicity. Whereas hitherto the emulsion had been prepared with as little delay as

was compatible with allowing the chemicals employed to react upon each other, it was found that in proportion to the time allowed for such reaction to take place so was the gain in sensitiveness within certain limits.

A further stage in this discovery was reached when it became known that the protracted action of several days' preparation of the emulsion might be condensed into that of a few hours by merely increasing the heat considerably beyond that at which liquefaction of the Gelatine was effected, and that consequently by varying the intensity of the heat and duration of exposure to it either a quick or a slow working emulsion could be prepared.

The foregoing is believed to be all that is necessary to be given here of a historical nature; minor details will be noticed as we proceed with practical directions for preparing and using the emulsion.

The first thing requisite is a suitable Gelatine. Nelson's Gelatine has acquired a deservedly high reputation in this connection, but in the hands of some it is found to be somewhat soft and apt to pucker up during subsequent stages of the manipulation, a tendency which is overcome by the admixture with it of a harder sample, that of the French brand "Coignet's" being much preferred for the purpose; but we have known a kind of Gelatine which was quite unfitted for emulsion work owing to its softness and solubility, having been rendered quite good by the admixture with it of Chrome Alum, an addition which, for this purpose, requires to be made with extreme caution and by very minute quantities, otherwise the gelatine will not only be rendered hard, but quite insoluble. This is of less importance when all the emulsion made at a time is to be used at once in the coating of plates without allowing it to become cold. An excess is discoverable by permitting a small portion to congeal or solidify and then noticing whether or not it has become insoluble. It is no secret that several manufac-

turers of plates add alum pretty freely to their emulsion in order to ensure a hard film and one which will not pucker up.

Allusion has been made to the "instantaneous" photographing of steamers and ships in motion from the deck of another steamer under full way. A detailed account of the method by which the emulsion was made and the plates prepared for that occasion will form a useful practical lesson at this juncture. It is proper to state that, although these plates are much more sensitive than wet Collodion, they are not the most sensitive that *can* be prepared. As regards certainty and reliability, however, they are altogether unsurpassed. Into a quart beaker place :—

Bromide of Ammonium .	200 grains
Nelson's No. 1 Gelatine .	80 ,,
Water	3 ounces

and allow to stand for a quarter of an hour, by which time the Gelatine will be swollen from its absorption of the water. It is well to dissolve the bromide previous to adding the Gelatine. At the end of the time specified place the beaker in a saucepan of boiling water, and as soon as the Gelatine is liquefied, which will be the case as soon as it becomes warm, the saucepan is removed into a dark room, and the remainder of the manipulations performed by ruby light.

A solution of Nitrate of Silver must in the meantime have been prepared of the following strength :—

Nitrate of Silver	330 grains
Water	3 ounces

and of this about half an ounce is poured into a graduate and diluted with half an ounce of distilled water, after which it is added to the Gelatine solution and well mixed with it.

There are various appliances by which the admixture may be thoroughly made, and much ingenuity has been expended in devising such appliances, but one of the best

consists in having a piece of a tolerably coarse and long-toothed vulcanite comb, of a length somewhat less than the diameter of the beaker, attached to a round wooden handle ten or twelve inches in length, much in the fashion of a miniature garden rake, with this difference, that the teeth will be standing in the same direction as the handle. This is placed in the Gelatine solution, and by rolling the handle between both hands a twirling motion is imparted by which the silver solution is rapidly incorporated with the Gelatine. After this addition allow the beaker to remain undisturbed for about a minute, then add the remainder of the silver in four or five doses, without diluting it as in the case of the first silver added, and with a vigorous application of the agitator after each addition.

The saucepan having been placed upon a gas stove in the dark room, the Gelatine emulsion is allowed to remain under the influence of the high temperature for three-quarters of an hour. This time may be shortened and a good emulsion be still eventually obtained, but it will be much less sensitive than if allowed to remain for the time mentioned.

By lowering the temperature of the water in the saucepan from the boiling point recommended to 150° Fahr., and greatly prolonging the time during which emulsification is allowed to take place, an equal degree of sensitiveness will be obtained. It may here be observed that several manufacturers prefer a moderately prolonged "cooking" at a medium temperature to a quicker one in boiling water.

Seeing that the ultimate sensitiveness and quality are so greatly dependent upon the duration of the exposure to the heat, it is of great consequence to manufacturers and others who wish to prepare plates which shall at all times maintain a reputation for equality and uniformity of sensitiveness to note carefully the time of "cooking" the emulsion to secure the best effects, and then to adhere strictly to it ever afterwards.

The beaker with its contents having been removed from the hot water, the emulsion is allowed to cool down to 100° Fahr. or a little over that temperature. There is then added to it a plain solution of Gelatine which has been prepared during the time the afore-described operation has been going on. It is composed of:—

French (Coignet) Gelatine .	½ ounce
Nelson's	½ „
Water	6 ounces

This is liquefied by first soaking together and then applying heat in the manner already described. No more heat is applied than suffices to cause its perfect liquefaction. The addition of this Gelatine solution to the emulsion, neither of them being much above 100° Fahr., is followed by an application of the agitator to ensure perfect admixture.

The beaker is now, with its contents, placed in a perfectly light proof box or case, and allowed to stand for several hours, or until the emulsion has become a cold firm jelly, which consists of Gelatine, Bromide of Silver, and Nitrate of Ammonia. To eliminate the last of these, the jelly must be washed in cold water into which a few small pieces of ice may advantageously be thrown to ensure a low temperature. The most convenient way by which to wash the emulsion is to place it, previously cut into pieces of convenient dimensions, into a thin porous canvas cloth sixteen or eighteen inches square, then twist the neck and immerse it in the cold water. So much pressure must be applied as to cause the emulsion to be forced out through the meshes of the canvas, by which it is broken up so completely as to enable the water to dissolve all the soluble Nitrate of Ammonium, which is effected partly by the direct action of the water upon the now large surface exposed, and partly by a species of dialysis in which the shreds of jelly form the septum for the separation of the soluble salts contained in their

substance. After a quarter of an hour the water is poured off, and the jelly again forced through the canvas into fresh water, in which it may be allowed to remain for half an hour. A third washing under similar circumstances will prove sufficient. The emulsion is next freed from the water as completely as possible by draining, and is then gathered together in the beaker, subjected to as low a degree of heat as suffices to liquefy it, and an ounce of Alcohol then added, together with as much warm water as will make up the volume to twenty ounces. After being stirred and filtered through muslin the preparation of the emulsion is completed, and it is now ready for use in coating plates.

As above described, the emulsion made will yield plates of a very satisfactory nature, both as regards sensitiveness and quality of mixture, but numerous deviations may be made from it in the apparatus employed, the methods of operating, the proportions of the ingredients employed, and in the substitution of others, and some of these we shall now refer to.

We have alluded to certain points of distinction between the Nelson and the Coignet Gelatines. It has been found to be a characteristic of the former that it has a slightly alkaline initial reaction which becomes more pronounced after being kept at a temperature of about 100° Fahr. for a few days. It is also found to lose to a considerable extent its power of setting by such treatment. It is possible for Gelatine to lose this power of setting without any decomposition having set in, but there is no doubt that prolonged "cooking" at a high temperature induces putrefactive decomposition. By this cooking the first change that takes place is the splitting up of Gelatine into two substances, Semi-glutin, insoluble in Alcohol and precipitated by Platinic Chloride; and Hemi-coline, which is soluble in Alcohol and not affected by Platinic Chloride (Eder). This splitting up is different from putrefaction.

A very high degree of sensitiveness is obtained when

by an exposure to a pretty smart heat as described in the directions above given for preparing emulsion, a slight decomposition has set up. This, while favouring sensitiveness, is hostile to setting or jellifying, hence the necessity for adding to the "cooked" Gelatine emulsion a large proportion of Gelatine which has not, by prolonged exposure to heat, lost this property. This shows in what manner the sensitiveness obtained by long cooking of several days' duration has its equivalent in an exposure to a higher temperature for a brief period.

Knowing that Ammonia is formed as a product of that prolonged heating which induces sensitiveness, it has been proposed to add Ammonia to the emulsion, both in a direct manner and also indirectly by means of Ammonio-nitrate of Silver, which is an Oxide of Silver dissolved in Nitrate of Ammonia, and in this way to secure a still higher degree of sensitiveness. The results hitherto obtained by this modification have not yet been such as to lead to a desire to abandon the simpler method. Nothing has yet surpassed the system of emulsifying with a soft and soluble Gelatine, one which, if not alkaline at the starting, becomes so after being in solution for a brief period, passing into a state in which the setting point is lowered several degrees after the slight boil to which it has been subjected, and then making an addition of a hard sample which is more slowly absorbent of water and sets at a tolerably high temperature.

There are some kinds of Gelatine which have not in process of manufacturing been rendered altogether free from fatty matter, by which defects are alleged to be caused in the Negatives. Such defects usually disappear by the addition of Ammonia to the emulsion, by which a saponaceous compound is formed that does not appear to be detrimental to the general working.

An exceedingly hard Gelatine is not favourable to the obtaining of a high degree of sensitiveness, that is

when the emulsification has been effected with such a kind. It is less amenable to the decomposing action of the heat during the emulsification. Hard, and by comparison non-porous, Gelatine approximates more nearly to a Collodion film, which has not yet been found to compare with Gelatine in sensitiveness, unless when, under certain conditions described in another place, an addition of Gelatine has been made to it in presence of a solvent common to both Pyroxiline and Gelatine.

We shall now describe a modification of the method already described in which the Bromide of Ammonium and plain Nitrate of Silver are supplanted by Bromide of Potassium and Ammonio-nitrate of Silver. The sensitiveness of the emulsion thus obtained is several times in excess of that secured by wet Collodion.

In a beaker place:—

Bromide of Potassium . .	370 grains
Gelatine	615 „
Water	10 ounces

The precise kind of Gelatine is here immaterial, but it is not advisable that it be alkaline. After allowing it to soak for some time, as in the previous formula, liquefy by placing the beaker in water of 105° Fahr. Now add by little at a time, and shaking or stirring after each addition, the following:—

Nitrate of Silver . . .	462 grains
Water	10 ounces

to which has been added (after solution) enough Ammonia, drop by drop to just barely dissolve the precipitate which is at first thrown down by the addition of the Ammonia. When the liquid is once more clear, pour in, as just directed, and allow the emulsion to cool down to 95° Fahr. The Silver should be rinsed out of the vessel in which it was dissolved by fourteen drachms of water which is then added to the emulsion. During the foregoing operation the emulsion may have

been removed from the water bath, the vessel containing it is once more immersed and the temperature raised to 95° Fahr., and then allowed to cool down gradually to the temperature of the room, after which the emulsion, subject to filtration, is ready for use.

Concerning the washing of the jellified emulsion to remove from it the crystallizable salts formed by decomposition during the preparation, there are four ways by which this may be effected—viz., by precipitation of the gelatine emulsion by alcohol; by the breaking up of the emulsion into small filaments in the manner already described, and which we prefer to any other; by dialysis, and by a more simple washing, which will be first described.

In this, the emulsion is poured out into a large flat dish to the depth of about a quarter of an inch. It is then allowed to become cold and firm, when it is broken away from the sides and bottom of the dish by means of a bone or horn spatula, a common paper-knife being much used for the purpose. After having been subjected to several changes of water during a period extending over a few hours, the emulsion is finally drained and liquefied by heat. By this treatment all the soluble salts will have been removed.

When dialysis is employed to effect the same purpose, the best form of dialyser consists of a porcelain or glass ring of about four inches in depth and of a diameter to suit the quantity to be operated upon. One that we have employed successfully is six inches in diameter. For small quantities, a porcelain jelly pot having its bottom knocked out makes a good extemporised dialyser. Over the bottom is stretched vegetable parchment as tightly as possible and retained in its place by either a piece of string or a rubber band. A large vessel containing warm water, about 105° Fahr., having been got ready, the dialyser is placed in it and supported in such a manner that the liquid emulsion when poured into it shall have its surface on a level with that of the water outside, and that

a depth of several inches of water shall be below its bottom. When covered up and allowed to stand in repose, by a process of osmose all the crystallizable salt present in the emulsion passes out through the parchment septum into the water, which ought to be changed two or three times during the process. There is a very simple method by which it may be ascertained whether the salts have been removed; if a little of the emulsion be at first spread upon a plate of glass the presence of the crystalline salt will be apparent upon drying it; by making a second trial after half an hour its presence will be much less marked; a further trial at a more advanced stage showing a total absence of the salt.

In preparing plates for coating, the question of a substratum requires a little consideration. Some kinds of Gelatine give a film which has a strong tendency to pucker up and leave the glass during subsequent treatment of the Negative. The tendency to move may be destroyed by coating the plate with a substratum. One of the best of these is found in an exceedingly thin film of insoluble Gelatine, which is easily prepared and readily applied. Dissolve 120 grains of any good Gelatine in a pint of water, and add to it five grains of Chrome Alum previously dissolved in a little water. This may be applied by means of a clean fine sponge. It leaves a thin and almost imperceptible film, which effects a strong union between the glass and the emulsion subsequently applied.

Highly diluted Albumen, about the white of an egg to a pint of water, is also used for the same purpose by many. One would at first sight imagine that the attenuated stratum of Albumen, being soluble in water, would be removed by the Gelatine emulsion in which water is the solvent, but the experience of many is given in attestation of its serving in a satisfactory manner the purpose for which it was applied. Powdered Steatite, or French chalk, which proves so useful in causing the adhesion of a Collodion film under similar

circumstances, is also used by some in connection with Gelatine.

Plates are most easily coated by means of a deep spoon which, when dipped into the vessel of emulsion, removes just so much as suffices for a plate of any determined size. The nature or form of the spoon may be conveyed by that of a soup-ladle, or a tobacco-pipe of clay or wood, the capacity being such as to hold emulsion enough for the area that is to be covered. By its agency, and keeping the emulsion at a uniform temperature during the operation, a few gross of plates may be prepared with absolute uniformity. It is convenient to have one such vessel or spoon for each size of plate that is coated, with the dimensions of the plate written on the handle, such as 22 × 17, 12 × 10, 5 × 4, and so forth. By the exercise of dexterity, aided by a pneumatic plate-holder and a chisel-shaped piece of thin bone, vulcanite or any substance that may be made thin and flexible, the emulsion may be evenly and rapidly spread over the surface of the plate, which is then removed by an assistant and placed upon a board or slab previously levelled with care. If the weather is moderately cool, the emulsion sets rapidly, after which, but not until then, the plates may be either reared up or placed in a drying box in any position irrespective of level. If the manufacture of plates is to be conducted on a large scale, each maker will establish a routine system adapted to his own requirements and surroundings. It is well to bear in mind that after a Gelatine film has set it does not again liquefy unless it be exposed very soon to a temperature considerably higher than that at which the setting took place. As coldness favours rapid setting, expedients may be had recourse to during hot weather to lower, by means of crushed ice and salt, the temperature of the atmosphere surrounding the setting slab upon which the plate is placed after being coated.

The thorough drying of the plates may be effected either spontaneously in a dark room, or in a box

specially constructed for the purpose. The principle upon which such a box is constructed is such as to allow of a current of pure air to pass over the surface of each, by which it is charged with moisture and passes off. The box must be tight, so as not to admit the faintest ray of light, and the shelves upon which the plates are placed must be so arranged as to allow the air, which is admitted at the bottom, to pass upwards in a zigzag manner, so as to expose the surface of each to the ascending draught. This current is caused by placing a lighted lamp of any construction requiring a large supply of air upon the top of the drying box, and contriving it in such a manner that no air can be supplied to the burner except what is fed to it through an aperture in the top of the box; hence, by igniting the lamp, an upward current of air is immediately started through the box and over the surface of the plates. Some have mistakenly reversed this order and placed the lamp below, allowing a current of air, heated and laden with the gaseous products of combustion, to have access to the plates. This is altogether wrong.

The various manufacturers pack their dry gelatine plates in various ways. Owing to the hardness of the film when dry, the same precautions against accident which are necessitated when working with Collodion plates are not here required. Some pack them face to back, others face to face without anything between them, others interpose between them a marginal slip of paper or thin card; but a way which we prefer to any is to have provided a supply of tissue paper cut in sheets the same dimensions as the plates, and the packing then done in the following order:—first a plate laid down face upwards, next a sheet of paper, then all the rest of the plates that are to form the package laid face down with a sheet of paper between each, with a primary wrapping of tissue paper followed by one of opaque paper. Plates so put up may be relied upon to remain quite good for a long time, certainly for several years.

Allusion has been made to the photographing of a

steamer in motion. This, however, is a feat which falls short of taking a perfect picture of the "Derby" race at the moment the horses are within a few feet of the winning-post, and are therefore at their utmost speed. Such a picture of the "Derby" of 1882 was taken by Mr. A. L. Henderson, and as this gentleman's methods differ somewhat from those of others, and of what we have described, he has kindly furnished the following details—never previously described in full—for this "Manual."

The Gelatine is neutral and not too soft, and he prefers emulsifying with a very small quantity of it.

Gelatine	30 grains
Bromide of Potassium . .	150 „
Iodide „ . .	2 „
Water	1 ounce
Alcohol	2 ounces
Ammonia (·880)	3 drachms

These are placed in a jar holding from 2 to 3 pints. The Bromide, Iodide, and Gelatine are first dissolved in the Water, after which the Ammonia and Alcohol, having been previously mixed, are added.

The heat having been raised to from 120° to 140° Fahr., an addition is made of—

Nitrate of Silver	200 grains
Water	2½ ounces

This is stirred in, after having been heated to the temperature of the other, in a fine stream.

After being allowed to stand for five minutes, the bulk of the Gelatine required (240 grains) is then added, dry, without any previous soaking in water. We may here premise that the Gelatine we saw used by Mr. Henderson is in very thin sheets. The heat remaining in the solution is quite sufficient to dissolve and properly emulsify the Gelatine last added.

The emulsion thus made is washed either in the usual way, or by precipitation with Alcohol, the latter

being preferred. To this end, 14 ounces of Alcohol, heated to a temperature of 100° Fahr., are slowly added, stirring all the time. The emulsion, if properly prepared, will be in a flocculent state, neither precipitating nor adhering to the stirring rod or sides of the vessel at first. It is now allowed to cool, by which time the emulsion will have become a cake at the bottom of the vessel. The liquid is now poured off, and the emulsion is removed from the bottom by means of a horn spoon, and placed under a small stream of water, which is allowed to trickle through it for a few hours. After this it is liquefied, and water added enough to make eight or ten ounces.

Those pictures we saw made were developed by the following :—

No. 1 (Stock).

Pyrogallic Acid	100 grains
Citric Acid	5 „
Water	10 ounces

The Citric Acid is dissolved previous to the addition of the Pyrogallic.

No. 2 (Stock).

Bromide of Potassium . .	2 drachms
Ammonia (·880)	1 ounce
Water	2 ounces

No. 3.

Water	1 pint
Of No. 2	2½ drachms

To develop : Take of No. 1, one drachm, and mix with seven drachms of No. 3, employing a dish for developing.

If, under any circumstances, intensification be desired, a saturated solution of Bichloride of Mercury, followed by diluted lime water, is recommended.

The variety of developers employed to suit various kinds of plates, or to gratify individual tastes, are such as would fill many pages of this "Manual" if here

given. In the formula of Mr. Henderson, just given, Citric Acid is present with the Pyrogallic in the stock solution to prevent oxidation. Sulphite of Soda is also extensively employed for this purpose. Mr. Berkeley, by whom it was first recommended, gives the following as a suitable proportion in which to use it:—In one ounce of water dissolve 200 grains of the Sulphite; then neutralize by an addition of a strong solution of Citric Acid, about four grains of the Acid sufficing; next add 50 grains of Pyrogallic Acid. This solution is of a ten-per-cent. degree of strength, and will remain colourless for months. Mr. Wilkinson makes his developer in a form which he believes to possess an advantage over that just given:—

No. 1.

Sulphite of Soda	4 ounces
Water	40 ,,

Dissolve, then add sufficient of a saturated solution of Citric Acid to produce a slight acid reaction upon litmus paper. Next add one ounce of Pyrogallic Acid, and make up the bulk to fifty-four ounces. Each ounce of this solution contains eight grains of Pyro.

No. 2.

Ammonia, ·880	1 ounce
Bromide of Potassium . .	180 grains
Water	40 ounces

Equal parts of Nos. 1 and 2, mixed together, give a four-grain solution suitable for developing.

In the developer of Mr. B. J. Edwards Glycerine is introduced with advantage.

Make two stock solutions, as follows:—

No. 1.

Pyrogallic Acid	1 ounce
Glycerine	1 ,,
Alcohol	6 ,,

Mix the Glycerine and the Alcohol, and add to the Pyrogallic Acid.

No. 2.

Bromide of Potassium . .	60 grains
Liquor Ammonia	1 ounce
Glycerine	1 „
Water	6 „

These stock solutions will keep a long time. To make the Developer, add one part of No. 1 to fifteen parts of water, and label this bottle D (Developer). In another bottle mix one ounce of No. 2 with fifteen ounces of water, and label it A (Accelerator). Either of these latter solutions will keep for two or three days. When required for use, pour into a clean glass measure equal parts of D and A, adding the A just before using. Place the plate in a flat tray, and pour the Developer over the surface, avoiding air bubbles. The image appears in a few seconds, and rapidly acquires strength.

Ferrous Oxalate Development.

Make a saturated solution of neutral Oxalate of Potash, and add a few crystals of Oxalic Acid, to ensure its being in a slightly acid condition, together with 20 grains of Bromide of Potassium for each pint of solution.

In another bottle make a saturated solution of Protosulphate of Iron, and add Sulphuric Acid in the proportion of about ten drops per pint.

When about to use it, mix one part of the iron solution with six parts of the Potassic Oxalate solution, and pour into a tray. The image appears slowly, and soon becomes very intense.

If greater rapidity in the development be desired, the proportions of the two mixtures may be varied; one of the Iron to four of the Oxalate being employed.

Fixing is effected by a nearly saturated solution of Hyposulphite of Soda.

Prolonged washing is requisite in order to get the fixing solution removed from the film.

Immersing the negative in a saturated solution of common alum is beneficial; it hardens the film and renders it less liable to frill, which sometimes takes place in very hot weather. This alum bath may be used after developing and before fixing.

Intensifying.—The plate should be washed and dried previous to its being intensified, should intensification be found necessary. The following modification of one of the oldest Collodion intensifiers is much employed :—

No. 1.

Bichloride of Mercury . .	60 grains
Water	6 ounces

No 2.

Iodide of Potassium . . .	90 grains
Water	2 ounces

No. 3.

Hyposulphite of Soda . .	120 grains
Water	2 ounces

No. 2 is poured into No. 1, and then No. 3 is added. The plate is immersed into the solution, which quickly imparts great density.

CHAPTER XIX.

THE COLLODION EMULSION PROCESS.

INSTEAD of going into the numerous ramifications connected with Collodion emulsions of various kinds, we shall here confine our remarks to the practical details of one good and thoroughly reliable process, the best of all that we have tried. It is essentially that of the late Mr. Henry Cooper. Mix together—

Bromide of Zinc . . .	80 grains
Lactate of Ammonia . .	20 minims
Plain Collodion	5 ounces

The Lactate of Ammonia is syrupy, and is prepared by neutralizing lactic acid with Ammonia.

Dissolve in a test tube 150 grains of Nitrate of Silver in about a drachm of water by the aid of heat, and add three ounces of Alcohol. Raise the heat to near the boiling-point, and pour the solution slowly and with agitation into the Collodion (in the dark). Keep in a warm place, and shake up at frequent intervals. After a day add twenty drops of Nitric Acid, shake well, and pour out into a flat dish to set. When nearly solid break up the thick film with a paper-knife and wash well with water, which must be changed several times. After drying, dissolve the pellicle in a mixture of five ounces of ether and five ounces of strong Alcohol.

This emulsion keeps well, and produces images of a very high class. The plates are coated, dried, and then stored away ready for exposure.

A useful developer for a Collodion emulsion plate is composed by—

A	Pyrogallic Acid . . .	3 grains
	Water	1 ounce

B { Bromide of Potassium . 10 grains
 { Water 1 ounce

C { Carbonate of Ammonia . 30 grains
 { Water 1 ounce

To every half-ounce of A add two drops of B and three drops of C.

The Negative is fixed with either Cyanide of Potassium or Hyposulphite of Soda.

Dry Bath Plates.—Dry Collodion plates may be prepared by the bath by sensitizing as usual and then thoroughly washing off the Nitrate of Silver. A preservative is then applied, which may consist of one or other of the following:—A fifteen-grain solution of tannin; a strong decoction of coffee; a solution of gum; a wash of Pyrogallic Acid with or without gum; or Albumen diluted with an equal part of water. If the last be used the plate should be immersed in hot water for a few seconds to coagulate the Albumen. All these preservatives yield plates less sensitive than those prepared by the emulsion described above.

CHAPTER XX.

WILLIS'S PROCESS FOR ENGINEERS' PLANS.

This process is different from other methods, inasmuch as it produces a positive from a positive, and *vice versâ*. Hence, it is eminently adapted for the reproduction of engineers' plans and drawings without the aid of a Camera. It is based on the fact, long ago ascertained, that Aniline with Chromic Acid strikes a deep blue colour.

Paper.—Select a thick, smooth-surfaced, and highly-sized plain paper. The thickest quality of *Saxe* will be found about the best that can at present be obtained, but it can still better be adapted for this purpose by hot-pressing each sheet before applying the Chemicals. The object of hot-pressing is to compress the fibre into the most compact state, and thus to keep the chemicals as much as possible on the surface.

Sensitizing Solution :—

Bichromate of Ammonia .	50 grains, or less.
Phosphoric Acid (solution)	1 drachm (fluid),
Water	1 ounce.

The Phosphoric Acid to be used in the above formula is the tribasic form, not readily obtained at an ordinary chemist's shop, except in a very dilute form, and of uncertain strength. The following indications will guide the operator as to the strength or quantity of his Phosphoric Acid. If too little acid is present the picture will develop of a reddish tint ; if too much, the colour will be green. The best tint is a purplish-black, obtained by regulating the acid according to the above indications of colour. Yet, after all, one need not be very particular on this point, because the colour can be afterwards changed.

To Sensitize the Paper it is pinned down by the corners to a drawing-board, and the above solution is spread over its upper surface evenly with a broad camel's-hair brush, or otherwise, and dried quickly by the fire or in a warm room. The object of drying quickly is to prevent the solution from penetrating far into the paper. The colour of the dried surface should be of a deep and uniform orange tint.

The sensitive papers should, if possible, be used during the same day on which they are prepared. If kept for twenty-four hours or upwards, a considerable diminution of sensitiveness is apparent, and often they will not take the aniline vapour uniformly.

The Exposure varies according to the intensity of the light and the resisting medium of paper, &c., through which the light has to be filtered. The transparent or translucent picture is laid on the glass of the printing frame, and the surface of the sensitized paper is pressed in contact, just as in the ordinary printing process. The proper time of exposure is not, however, so readily detected by the eye as in silver prints; but a very short experience will render the matter easy. When exposed for the proper time, a well-defined outline of all the *dark* portions of the print should be apparent in orange colour on a darker ground. Generally speaking, the time of exposure is about one-fifth of that required for the same subject on the most sensitive silver-chlorized paper. But the indications of over-and under-exposure are easily discerned when we come to the—

Development.—A shallow wooden box (about two inches deep) with a lid of the same material, forms a very convenient developing dish. Pin to the inner surface of the lid two or three folds of bibulous paper. Moisten them with a solution composed of common commercial Aniline (four drachms), and Benzol (two ounces or more). About a drachm of this mixture will be sufficient to develop a print about two feet square. Place inside, on the bottom of the box, as many prints as

will lie thereon, but not on the top of each other. Put on the lid. In about twenty minutes, more or less, the whole should be fully developed by the vapour of Aniline falling upon them. Now is the time to examine for over or under-exposure. If the exposure has been a little too long a feeble green, blue, or reddish image (the colour depending to a great extent on the amount of Phosphoric acid in the Bichromate) will be perceptible. But if the time of exposure has been greatly exceeded, no image at all, or at least a very feeble one, will be apparent, because the light has had time to penetrate through the dark parts of the intercepting medium and decompose the Bichromate.

The symptoms of under-exposure are just the reverse. In such cases the exposed papers develop all over, so to speak, the high lights being discoloured by the Aniline vapour nearly as readily as the shadows.

The development being complete, it is of little consequence whether the resulting image be red, green, or blue. The tone can be changed in the simplest manner. But before doing so it is advisable to *fix* the picture by washing off the soluble salts. This is done in common water. Immerse the print in water acidulated with Nitric or Sulphuric Acid; quickly the original colour, whatever it may have been, will change to a deep bluish green. Wash the print and again immerse it in water containing a few drops of Ammonia, when, almost instantly, the picture turns a rosy-purple shade. Try the acid again. The green will be deeper than before. Wash once more, and immerse in a weak solution of Ferrocyanide of Potassium; then the green will be of the most delicate spring-leaf kind. These chameleon-like changes of colour may be made over and over again; but the most remarkable fact connected with them is, that after every change the colours are much improved, and a greater general vigour is imparted to the image.

CHAPTER XXI.

MICRO-PHOTOGRAPHY.

SELECT a window facing south or south-west, throw it open, place a *firm table* near to it, fix the microscope at one end of a 4 or 5 feet stout deal clamped board resting on the table, and so arrange the instrument that, when turned horizontally, the sun's image may be thrown by the mirror or prism, set at a right angle to the path of the rays, through the axis of the instrument, the objective and eye-piece being removed. Select the camera to be used, and so place it on the board that the eye-piece end of the microscope may be passed through the centre of a stout cardboard cap, or brass tube lined with cloth, made to take the place of the ordinary brass cap of the camera combination, the cells carrying the lenses having been unscrewed. Receive the image of the sun on the ground-glass screen, observing that the spot of light occupies its centre, firstly throwing the ordinary focussing cloth over the end of the camera and microscope, so as to totally exclude any light admitted into the camera by the side of the tube of the microscope. Now attach a low power objective to the microscope, and note if the sun's image remains central on the focussing screen; if not, adjust the mirror, camera, and microscope until this be determined, then mark the position of the camera and microscope on the deal board, and clamp them there. Select the object to be photographed, place it on the stage, as usual (it is better generally to narrow the central aperture of the stage to nearly the size of the object by a pierced card blackened or black paper gummed to the under side of the slide), and shut up the camera so that with the hand on the coarse rack

adjustment it may be focussed at the same time as the head is inclined towards the focussing glass, so that with the focussing cloth thrown over it, the eye may note the definition, size of the image, and equality of the illumination. Should it be determined to use the ull range of the camera, some arrangement for working the rack movement will be necessary, such as a rod attached at its opposite end by a lever or grooved wheel, connected by a band to the milled head of the coarse or fine rackwork. Suppose the sensitive plate prepared and ready to be dropped with its carrier into the camera, note that the illumination is perfect, then shut off the light by any simple plan; insert the carrier, draw up the shutter, and apportion the period of exposure to the colour of the object, the distance of the screen, the brightness of the light, and condition of the chemicals or sensitiveness of the plate; this may range from one to several seconds. The Negative, when developed and cleared, may show a very imperfect or ill-defined image from the want of coincidence of the visual and actinic foci of the objective, which for that distance may be ascertained by tentative trials, withdrawing the objective from the object by a turn or part of a turn of the fine adjustable milled head, or what is perhaps preferable, by having a suitable thin convex, long focus, spectacle lens, ground down and fitted into a cell which screws into the place of the back stop of the objective. The focus of the lens required may be from 8 to 12 or 14 inches; or a large cell with parallel glass slides, containing a deeply-coloured solution of ammonio-sulphate of copper, may be placed between the mirror and the stage, to shut off the non-actinic rays. Some of the low powers are found to have their chemical and visual foci so nearly coincident that they require no extra adaptation. The actual position of the objective for a given distance once found, a mark may be made on the board at which the sensitive plate was placed, to save further trouble.

With medium powers more care is required, and the adjustment collar for the thickness of the cover must be attended to; what is needed in the objective being rather under correction for colour though correct for spherical aberration, which latter alters with the distance between the object and image. Generally some form of condenser is necessary to concentrate the light from the plain mirror or prism. These are of various kinds, and are used as in the ordinary conditions of the microscope, but it has been found best to employ lenses of some size, of course taking care that the focus is so arranged as not to scorch the object. In some cases there is a difficulty in getting rid of the diffraction lines at the edges of objects, and then a cap containing a piece of ground glass in a cell, slipped over the top combination of the achromatic condenser, and so placed as to become a bright radiant of softened sunlight wherewith to illuminate the object, is found to have great advantages, though the time of exposure is increased.

With high powers, the visual and actinic foci so nearly approximate that they are often used as if really coincident; but even here it will be found a better plan to insert the ammonio-sulphate of copper cell, or else to use a prism of some considerable dispersive power, and illuminate the object by the violet end of the spectrum. At the same time as the powers increase, it becomes very important to employ an examining glass, as a Ramsden's positive eye-piece, for the best point of the image as regards definition on the focussing screen, or even to substitute for the ground glass a polished piece of plate glass, Dr. Woodward's method, always remembering that the more enlarged the image, the less sharp will it appear; moreover, it is objectionable to strain the lens to work beyond its suitability, or to use the eye-piece with it without especial care.

If a heliostat be employed for this form of apparatus, it may be placed on the window sill, having taken the necessary precautions for its position as regards the sun

and its correct level; or, it may be fixed to the side of the top of the front part of the camera. Much good work can be done without it if the chemicals be in good working order. With high power immersion lenses the time of exposure is lessened, and they have other advantages; but whatever means may be taken to illuminate the object, it is absolutely necessary the whole *apparatus remains free of vibration.* Indeed, after lifting the shutter of the camera, it is as well to pause before removing the card from the stage or objective.

CHAPTER XXII.

THE OPTICS OF PHOTOGRAPHY.

ON THE NATURE AND PROPERTIES OF LIGHT.

Although in a Manual like this an elaborate disquisition on Optics would be as much out of place as one on Chemistry, yet it is considered desirable that such an account be given of the nature and properties of Light, as applied to Photographic Lenses, together with an account of the construction and uses of such Lenses, as shall enable the reader to acquire a clear idea of the most important of all the appliances involved in the production of a picture.

SECTION I.

The Compound Nature of Light.

The ideas entertained on the subject of Light, before the time of Sir Isaac Newton, were vague and unsatisfactory. It was shown by that eminent philosopher, that a ray of sunlight was not *homogeneous*, as had been supposed, but consisted of several rays of vivid colours, united and intermingled.

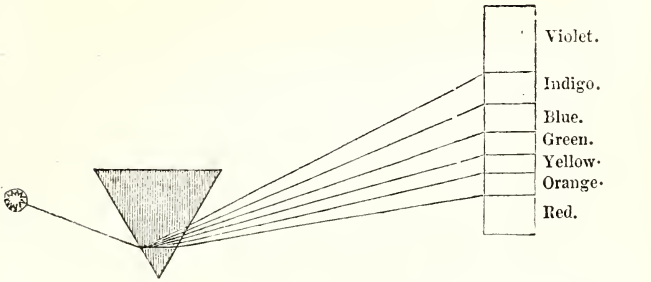
This fact may be demonstrated by throwing a pencil of sunlight obliquely upon one side of a *prism*, and receiving the oblong image so formed upon a white screen.

The space illuminated and coloured by a pencil of rays analysed in this way is called "the Solar Spectrum," in which seven principal colours may be distinguished in the Solar Spectrum—viz., red, orange, yellow, green, blue, indigo, and violet. Sir David Brewster has made observations which lead him to

suppose that the *primary* colours are in reality but three in number—viz., red, yellow, and blue, and that the others are *compound*, being produced by two or more of these overlapping each other; thus the red and yellow spaces intermingled constitute *orange;* the yellow and blue spaces, *green.*

The composition of white light from the seven prismatic colours may be roughly proved by painting them on the face of a wheel, and causing it to rotate rapidly: this blends them together, and a sort of greyish-white is the result. The white is imperfect, because the colours employed cannot possibly be obtained of the proper tints, or laid on in the exact proportions.

Fig. 15.



The decomposition of light is effected in other ways besides that already given:—

First, by *reflection* from the surfaces of coloured bodies. All substances throw off rays of light which impinge upon the retina of the eye and produce the phenomena of vision. Colour is caused by a *portion only*, and not the whole, of the elementary rays, being projected in this way. Surfaces termed *white* reflect all the rays; coloured surfaces absorb some and reflect others; thus *red* substances reflect only red rays, *yellow* substances, yellow rays, etc., the ray which is reflected in all cases deciding the colour of the substance.

Secondly, light may be decomposed by *transmission*

through media which are transparent to certain rays, but opaque to others.

Ordinary transparent glass allows all the rays constituting white light to pass; but by the addition of certain metallic oxides to it whilst in a state of fusion, its properties are modified, and it becomes *coloured.* Glass stained by Oxide of Cobalt is permeable only to blue rays. Oxide of Silver imparts a pure yellow tint; Oxide of Gold or Suboxide of Copper a ruby red, etc.

PROPERTIES OF LIGHT.

Light possesses a threefold property—viz., heating, illuminating, and chemical action, now usually termed Actinism. These properties have up to a recent period been associated with certain rays; for example, the yellow ray is popularly spoken of as that in which resides the illuminating power; the red being said to be the heating ray, and the violet or blue the chemical. But this is true only in a certain limited sense, especially as regards the chemical action of the blue rays. While it is the case that certain salts of Silver, such as the Chloride, become darkened by the blue rays, while they do not undergo visible change by similar exposure to the red or yellow. Yet is it now known that other salts of the same metal, when exposed to the Solar Spectrum, are more quickly changed by the red than by the blue. Examples of this will be found adduced in the chapter on Heliochromy, or the production of Photographs in natural colours.

It is correct to say that all the rays induce chemical change, although in the chemicals employed in the ordinary practice of Photography those in the region of the blue and violet end of the Spectrum are the most active. In the early days of the art, before the value of Bromine as a Photographic agent became known, yellow and red were almost synonymous with black, while articles of a blue colour appeared white in the Photograph. This is now no longer the case.

All who desire to become thoroughly acquainted with the properties of light in connection with Photography, should possess facilities for projecting the Solar Spectrum upon the table at which they operate. This is readily accomplished by admitting a ray of sunlight through a small aperture in an opaque window shutter, and interposing in its path a triangular glass prism, by which the beam will be decomposed into the prismatic colours, and be deflected out of its course. A thermometer placed in the Spectrum thus formed rises most rapidly in the red rays; the yellow gives the highest degree of illumination, as proved by the sense of sight, while a piece of sensitive Photographic paper, as commonly employed in printing, undergoes no change in the red, scarcely any in the yellow, but darkens with great rapidity in the violet.

REFRACTION OF LIGHT, AND LENSES.

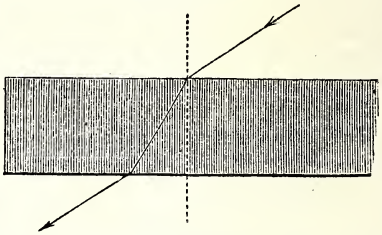
A ray of light, in its passage through any transparent medium, travels in a straight line as long as the density of the medium continues unchanged. But if the density varies, becoming either greater or less, then the ray is *refracted*, or bent out of the course which it originally pursued. The degree to which the refraction or bending takes place depends upon the nature of the new medium, and in particular upon its density as compared with that of the medium which the ray had previously traversed. Hence Water refracts light more powerfully than Air, and Glass more so than Water.

The following diagram illustrates the refraction of a ray of light:—

The dotted line is drawn perpendicularly to the surface, and it is seen that the ray of light on entering is bent *towards* this line. On emerging, on the other hand, it is bent to an equal extent, *away from the perpendicular*, so that it proceeds in a course parallel to, but not coincident with, its original direction. If we

suppose the new medium, in place of being more dense than the old, to be *less dense*, then the conditions are exactly reversed—the ray is bent away from the perpendicular on entering, and towards it on leaving.

Fig. 16.



It must be observed that the laws of refraction apply only to rays of light which fall upon the medium at *an angle:* if they enter perpendicularly—in the direction of the dotted lines in the last figure—they pass straight through without suffering refraction.

Notice also, that it is *at the surface of bodies* that the deflecting power acts. The ray is bent on entering, and bent again on leaving; but whilst within the medium it continues in a straight line. Hence it is evident that by variously modifying the surfaces of

Fig. 17.

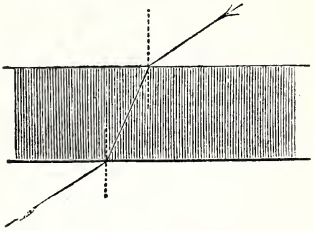
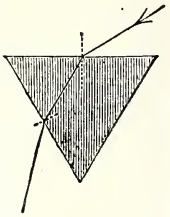


Fig. 18.



refractive media the rays of light may be diverted almost at pleasure. This will be rendered clear by a few simple diagrams.

In the figures following the dotted lines represent

perpendiculars to the surface at the point where the ray falls, and it is seen that the usual law of bending *towards* the perpendicular on entering, and *away* from it on leaving the dense medium, is in each case correctly observed.

Fig. 18, in the last page, termed a prism, bends the ray permanently to one side; fig. 19, consisting of two prisms placed base to base, causes rays before parallel to meet in a point; and conversely, fig. 20, having

Fig. 19.

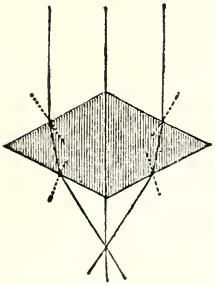
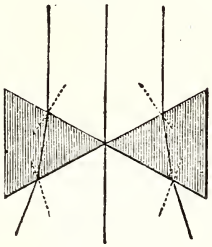


Fig. 20.



prisms placed edge to edge, diverts them further asunder.

The various Forms of Lenses.—The phenomena of the refraction of light are seen in the case of *curved* surfaces in the same manner as with those which are plane.

Glasses ground of a curvilinear form are termed *Lenses.* The figures given on the following page are examples.

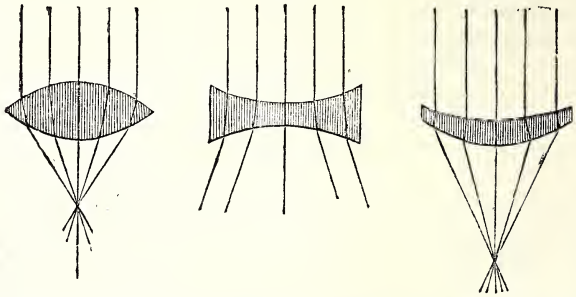
Fig. 21 is a biconvex lens; fig. 22, a biconcave lens; and fig. 23, a *meniscus* lens.

As far as regards their refractive powers, such figures may be represented, nearly, by others bounded by straight lines, and thus it becomes evident that a biconvex lens tends to condense rays of light to a point, and a biconcave to scatter them. A meniscus combines both actions, but the rays are eventually

bent together, the convex curve of a meniscus lens being always greater than the concave.

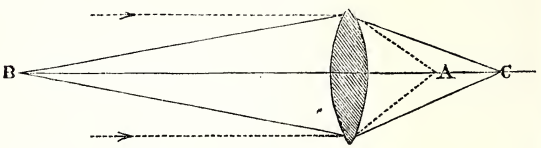
The Foci of Lenses.—It has been shown that convex lenses tend to condense rays of light and bring them together to a point. This point is termed "the focus" of the Lens.

Fig. 21. Fig. 22 Fig. 23.



The following laws as regards the focus may be laid down:—That rays of light which are pursuing a parallel course at the time they enter the Lens are brought to a focus at a point nearer to the Lens than diverging rays. The rays proceeding from very distant objects are parallel; those from objects near at hand diverge. The sun's rays are always parallel, and the divergence of the others becomes greater as the distance from the Lens is less.

Fig. 24.



The focus of a Lens for parallel rays is termed the "principal focus," and is not subject to variation; this is the point referred to when the *focal length* of a Lens is spoken of. When the rays are not parallel, but

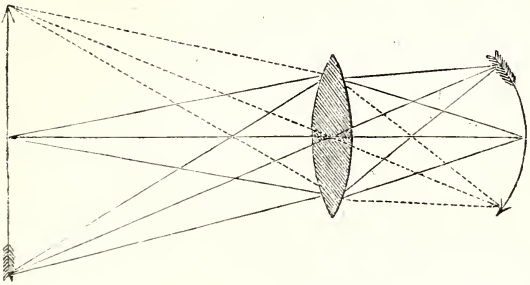
diverge from a point, that point is associated with the focus, and the two are termed "conjugate foci."

In the last diagram A is the principal focus, and B and C are conjugate foci. Any object placed at B has its focus at C, and conversely when placed at C it is in focus at B.

Therefore, although the principal focus of a Lens (as determined by the degree of its convexity) is always the same, yet the focus for objects near at hand varies, being longer as they are brought closer to the Lens.

Formation of a Luminous Image by a Lens.—As the rays of light proceeding from a *point* are brought to a focus by means of a Lens, so are they when they pro-

Fig. 25.



ceed from an object, and in that case *an image of the object* is the result.

In order that the course pursued by pencils of rays proceeding from an object may be easily traced, the lines from the barb of the arrow in the figure 25 are *dotted*. Observe that the object is necessarily *inverted*, and also that those rays which traverse the central point of the Lens, or the centre of the *axis*, as it is termed, are not bent away, but pursue a course either coincident with, or parallel to the original, as in the case of refracting media with parallel surfaces.

Enlarged and Reduced Images.—When an object is placed at some distance in front of a Lens an image is formed, smaller than the object; but if the object be advanced nearer to the Lens the image increases in size until it becomes, first equal to, and then larger than the original, the focus at the same time receding to a greater distance from the Lens.

Thus if a photographic portrait be approximated to a Lens an image of the life size may be thrown upon a screen, just as the rays proceeding from the living model were in the first instance employed to form the portrait. The two planes, in fact, of the object and of the image are strictly *conjugate foci* (p. 396), and it is immaterial from which of the two, anterior or posterior, the rays of light proceed.

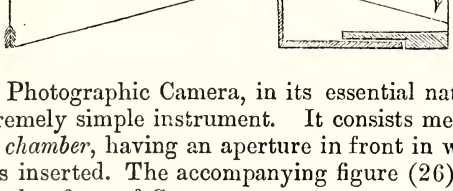
Amplifying instruments, like Woodward's Patent Solar Camera, are constructed upon the above principle, and are found useful in enlarging photographs to three or four times their original diameter. A loss of definition always results in this process, which may conveniently be remedied by the pencil of the artist.

Lenses of Long and Short Focus.—A Lens of short focus placed at a given distance from an object forms a small image, the rays being strongly refracted. If the Lens be brought nearer to the object, the image becomes larger, as above shown; but at a certain point the approximation must be stopped, or the Lens will be *strained*, as the opticians term it, and distortion will result. Therefore Lenses are purposely constructed of a longer focus when a large image is required.

Long-focus lenses for taking large pictures have usually a considerable diameter, but it will be understood that the size of a Lens has nothing whatever to do with the size of the image. *The focal length* of the Lens, at a given distance, determines the size of the image; nevertheless, since the luminous rays are diffused over a large space when the focus is long, the optician is compelled in such a case to increase the aperture of the glass in order to transmit more light.

The focal length of a single actinic combination is usually found by focussing a distant object, and then measuring the distance from the back of the lens to the refracted image on the screen. This distance represents the focal length of the lens. It is not strictly accurate, but near enough for all practical purposes. The focal length of a double or triple combination of lenses cannot be thus estimated, because the point from which it is measured is situated somewhere in front of the back combination; hence a more complicated process of measurement must be adopted to determine what is called in this case the "equivalent focus," or the distance from the screen, at which a single lens must be placed in order to give the same-sized image. This will be treated of farther on.

Fig. 26.



The Photographic Camera, in its essential nature, is an extremely simple instrument. It consists merely of a *dark chamber*, having an aperture in front in which a Lens is inserted. The accompanying figure (26) shows the simplest form of Camera.

The body is represented as consisting of two sliding portions; but the same object of lengthening or shortening the focal distance may be attained by making the Lens itself movable. A luminous image of any object placed in front of the Camera is formed by means of the Lens, and received upon a surface of ground glass at the back part of the instrument. When the Camera is required for use, the object is *focussed* upon the ground glass, which is then removed, and a slide containing the sensitive layer inserted in its place.

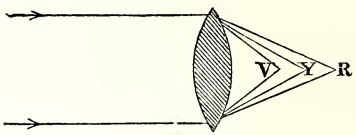
The luminous image, as formed upon the ground

glass, is termed the "Field" of the Camera; it is spoken of as being flat or curved, sharp or indistinct, etc. These and other peculiarities depending upon the construction of the Lens will now be explained.

Chromatic Aberration: Visual and Actinic Focus.—The outside of a biconvex lens resembles the sharp edge of a *prism*, and necessarily produces *decomposition* in the white light which passes through it. The luminous image of an uncorrected Lens, is in consequence bounded by coloured fringes.

The action of a prism in separating white light into its constituent rays may be simply explained. The indigo and violet rays are more bent away than the yellow and red, and consequently they are separated from them, and occupy a higher position in the Spectrum. (See fig. 27). A little reflection will show

Fig. 27.



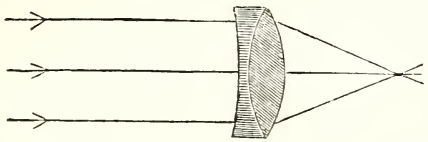
that in consequence of this unequal refrangibility of the coloured rays, white light must invariably be decomposed on entering any dense medium obliquely. This is indeed the case; but if the surfaces of the medium *are parallel to each other* the effect is not seen, because the rays recombine on their emergence, being bent to the same extent in the opposite direction. Hence light is transmitted colourless through an ordinary pane of glass, but yields the tints of the Spectrum in its passage through a prism or a lens, where the two surfaces are inclined to each other at an acute angle.

The same causes which produce chromatic aberration in a Lens, tend also to separate the chemical from the visual focus. The violet and indigo rays are more

strongly bent in than the yellow, and still more than the red; consequently the focus for each of those colours is at a different point. The preceding diagram shows this. V represents the focus of the violet ray, Y of the yellow, and R of the red. Hence, as the chemical action corresponds more to the violet, the most marked actinic effect would be produced nearly at V. The luminous portion of the spectrum however is *the yellow*, consequently the visual focus is at Y.

Photographers have long recognized this point; and therefore, with ordinary Lenses, not corrected for actinism, rules are laid down as to the exact distance which the sensitive plate should be shifted away from the visual focus in order to obtain the greatest amount of distinctness of outline in the image impressed by chemical action.

Fig. 28.



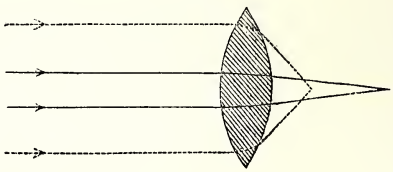
Actinic aberration is corrected by combining two lenses cut from varieties of glass which differ in their power of separating the coloured rays. These are generally the dense flint-glass containing Oxide of Lead, and the light crown-glass. Of the two lenses, the one is *biconvex*, and the other *biconcave*; so that when fitted together they produce a compound Actinic lens of a meniscus form, as shown in fig. 28.

The first Lens in this figure is the flint- and the second the crown-glass. Of the two the biconvex is the most powerful, so as to overcome the other, and produce a total of refraction to the required extent. Each of the Lenses is made from glass of different dispersive power to that of its coadjutor; and the effect

of passing the rays through both, is, by overlapping the coloured spaces, to unite the complementary tints, and to re-form white light.

Spherical or Axial Aberration.—Spherical aberration is the property possessed by Lenses *which are segments of spheres* of refracting rays of light unequally at different parts of their surfaces. The following diagram shows this in an exaggerated degree :—

Fig. 29.



Observe that the dotted lines which fall upon the circumference of the Lens are brought to a focus at a point nearer to the Lens than those passing through the centre; in other words, the outside of the Lens refracts light more powerfully. This causes a degree of confusion and indistinctness in the image, from various rays crossing, and interfering with each other.

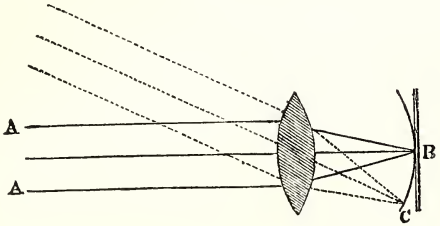
In correcting for spherical aberration, the first point to be attended to, is the curve of the Lens itself. A biconvex Lens, as shown in the above diagram, is the worst form. The Plano-convex and Meniscus Lenses are preferable, and for landscapes the latter is very commonly employed.

But spherical aberration, even in a Lens which is badly made as regards *form*, may be remedied in another way—viz., by using a diaphragm or stop, so as to cut off a portion of the light, and prevent the same pencil of rays from falling both on the centre and on the edge of the Lens. As the action of a stop is more fully explained a few pages in advance, we defer the further consideration of it for the present.

Curvature of the Field.—In using a Camera mounted

with a Meniscus Lens, it will be observed that when the centre of the field has been focussed, the outer portions of the image appear indistinct, whilst if the ground glass be pushed in a little, the outside becomes sharp, but the centre is thrown out of focus. This defect is sometimes attributed to spherical aberration, but incorrectly so, because indistinctness from that cause is seen alike at every portion of the field. The want of definition which can be remedied by shifting the position of the focussing-screen we refer rather to curvature of the field, or to the fact that the image of a flat surface, formed by a Lens, produces not a plane, but a portion of a *hollow sphere*, as shown by the inverted arrow, page 401.

Fig. 30.



In the above diagram the centre line running at right angles to the general direction of the Lens is the *axis;* an imaginary line, on which the Lens might be rotated as a wheel is turned on its axis. The lines A A represent rays of light falling parallel to the axis; and the dotted lines, others which have an *oblique* direction; B and C show the points at which the two foci are formed. Observe that these points, although equidistant from the centre of the Lens, do not fall in the same vertical plane, and therefore they cannot both be received simultaneously upon the ground glass of the Camera, which would occupy the position of the perpendicular double line in the diagram.

The defects due to curvature of the field might be

avoided by *bending* inwards the glass or paper used to sustain the sensitive Iodide, in such a way as to meet the image, as is done in the apparatus for Sutton's Panoramic Lens: but practically this plan, though possessing some advantages, is in other respects objectionable. The image itself therefore must be flattened out, and this can be effected by means of the diaphragms before alluded to in the paragraph on spherical aberration: the position and use of which will be shown in the following pages.

Variation of Focus for Near and Distant Objects.—Lenses employed with the full aperture, do not render near and remote objects sharp upon the ground glass of the Camera at the same time. If the foreground is in focus, the Lens must be thrown inwards to make the distance clear, and *vice versâ*. This is a necessary consequence of the focal plane of any object varying with the position of the object in regard to the Lens.

The action of a diaphragm or stop, already spoken of under the head of "Spherical Aberration" and "Curvature of the Field," is seen to still greater advantage in remedying the defect now complained of.

Fig. 31.

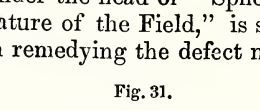


Fig. 32.

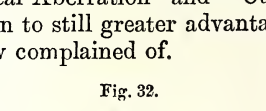


Fig. 31 represents rays of light radiating in all directions from a luminous point, and falling on the entire surface of a Lens; fig. 32, the action of the diaphragm in intercepting that portion of the rays which otherwise would impinge upon the outside of the glass. The focus in each case is at the point where the rays cross each other after refraction. Now in fig. 31 suppose the greyed screen, represented by the dotted line, to be advanced nearer to the Lens, or to be withdrawn from it, even in

the least degree, the image would immediately be out of focus; but in the second figure, the rays run so nearly parallel, that the effect of a slight change of position would not be perceptible. The refracted pencil is, as it were, sharpened and drawn out, so that the focus has considerable *depth*, and is no longer confined to a single plane. The first figure represents what is termed *a large angular pencil* of rays, and fig. 32 *a small angular pencil;* the latter alone can be employed when near and distant objects are to be simultaneously depicted.

The focal variation for near and distant objects is much more considerable when Lenses of very long focus are employed, and (always supposing the distance from the object to remain the same in the two cases) it becomes less evident with Lenses of short focus. Hence the small Lenses used for stereoscopic Photography have usually some depth of focus with a comparatively large aperture.

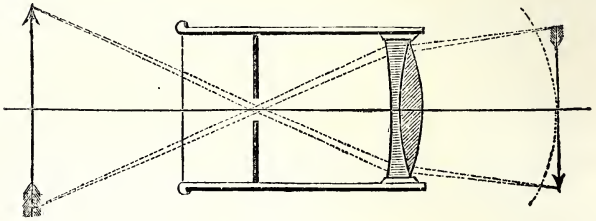
The optics of Photography differs from that of the telescope or microscope. It comprises the formation of an image of such objects as have an extended range from side to side, or above and below that point to which the lens is directed, such image to be formed upon a flat plate and made to cover an area of considerable extension. Telescopic optics, on the other hand, has relation to the formation of a sharp image in the axis of the lens only of any object situated in or near its axis, the sharpness being such as to permit of the image being examined through a powerful magnifier. While telescopic optics thus has reference to the axial transmission of light through a lens, in photographic optics, on the contrary, such conditions must be sought for as will secure the sharp distribution of a scene or figure over a certain area designated the field of delineation. To secure this, the light must be made to pass through the lens in an oblique as well as axial manner.

Photographic Lenses may be divided into four classes

—the single achromatic landscape lens, the portrait lens, the group or copying lens, and the wide angle non-distorting or architectural lens. Between each of these classifications it is difficult to draw a hard-and-fast line, seeing that some objectives are now constructed which fulfil more than one of the requirements named.

The Single Landscape Lens.—For ordinary landscapes no lens or form of objective has yet been introduced which surpasses the single achromatic lens, which,

Fig. 33.



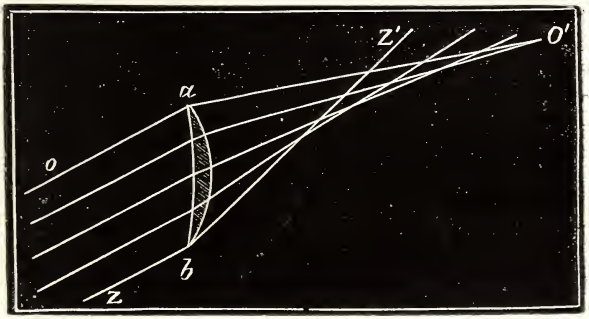
when properly constructed, gives pictures possessing sharpness and brilliance, includes a wide angle of subject, and works with a reasonable degree of rapidity. The form of the single achromatic landscape lens is shown in the adjoining cut, in which an achromatic meniscus is placed at one end of the tube, there being a diaphragm in front of it.

At this stage we may fittingly introduce a diagram which explains the useful part subserved by the diaphragm or stop when placed in front of a landscape lens.

In this diagram a number of rays, *o*, *z*, and those between them, are represented as impinging obliquely upon the flattest surface of a lens, L, all of them, however, taking different courses as regards their crossing each other after being transmitted. The image of any object would be quite devoid of sharpness, and

be hazy, owing to the ray z being refracted in a greater degree than any others of those between it and the upper boundary ray o. If the transmitted ray z, instead of taking the course z', went straight to o', the

Fig. 34.



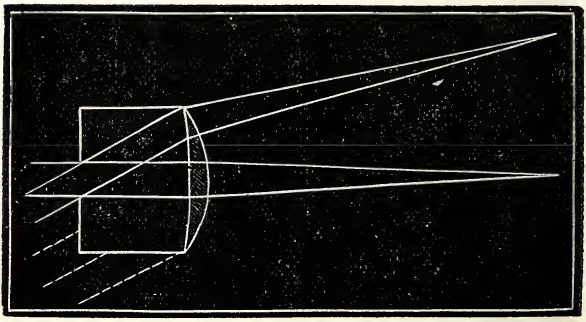
intermediate rays doing the same, then would we have a perfect single lens; but such is not the case, owing to the aberration caused by the spherical surface of the glass. Spherical aberration, it may here be once more remarked, is that property in a lens whereby parallel rays falling either obliquely or axially upon its surface undergo such different degrees of refraction as prevent them meeting at one point.

The function of a diaphragm as applied to a single achromatic lens having its flattest side next to the subject to be depicted, is to prevent any rays from having access to the lens but those which shall be transmitted, both axially and obliquely, to a pictorially sharp focus. The manner in which the diaphragm effects this is shown in fig. 35, on next page, in which the axial rays are transmitted to a sharp focus, the oblique rays, all but those which pass through the diaphragm and come to a focus as shown, being debarred access to the lens by the mounting and the diaphragm.

We shall hereafter speak of other functions of the

diaphragm. The subject is here introduced to show in what manner it becomes necessary to the correct working of a single-view lens, whether achromatized or not.

Fig. 35.

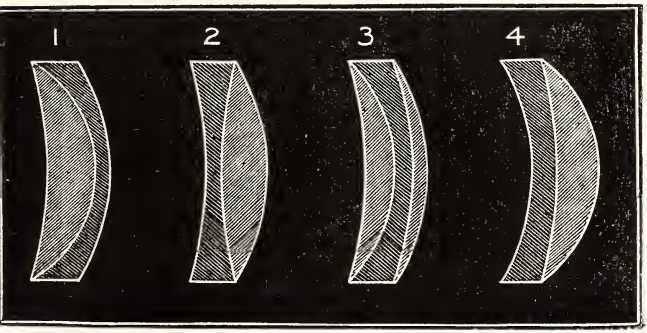


Lenses are achromatized by a judicious combination of a concave lens formed of flint glass with a crown glass convex, the respected degrees of curvature being so determined as to bring all the rays of the spectrum, at any rate the visual and more energetic of the chemical ones, to a focus. Were this not done, the plane at which by aid of the ground glass of the Camera the image was *seen* to be sharp would be somewhat distant from that plane at which the more violet rays were brought to their focus, and as the picture is produced by these latter rays it would necessarily be out of focus. By securing the coincidence of the chemical and visual focus, the picture which is depicted upon the ground glass or focussing screen of the Camera is that which is secured upon the chemically prepared surface of the sensitive plate.

The forms which the concave flint and the convex crown glass lenses are made to assume depend largely upon the ideas of respective makers, some preferring one form and some another. The systems in use by one or other of the leading lens-makers at the present time are those depicted in fig. 36 :—

In external form these are all alike, or nearly so; but when their interior construction is observed it is seen that all similarity ceases. Of these various methods of achromatizing a lens, the third and fourth are preferred

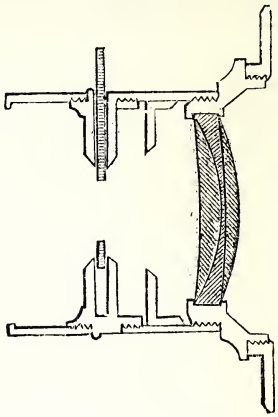
Fig. 36.



on account of their transmitting to a focus a larger pencil light than the others. The first, a bi-concave flint and a bi-convex crown, is the oldest form of achromatic lens, the second being merely an extension of the same principle of construction, to render the lens more of a meniscus form. The third shows an entirely different principle in the arrangement of the elementary parts, and is that now adopted in almost all of the "rapid" series of lenses which will be described in turn. In this, when employed as a single landscape objective, the light falls upon the crown instead of the flint glass, and the inner or contact surfaces are more nearly normal to the transmitted pencil than in the former forms of lens. The fourth is in a certain sense similar in principle to the third, but possesses this advantage, that the flint glass which is usually soft and liable to become scratched or otherwise damaged is enclosed between two crowns, and is the most perfect form of single achromatic landscape lens that has been constructed, and is shown fully mounted in fig. 37, which represents Dallmeyer's landscape lens. When a single

achromatic lens of the kind described—whatever its interior form of curvature—is required to include a very wide angle of view, or, in other words, to cover a large field in comparison with its focus, it is necessary that its exterior form be that of a deep meniscus and that the diaphragm be placed somewhat near to the first surface. This permits of the transmission of extremely oblique rays. When the meniscus form is very pronounced, a smaller diaphragm is required to correct the spherical aberration than with an objective more nearly approaching a plano-convex, in which latter case a larger aperture may be employed, thus securing greater rapidity of action but on a less extended field. The best single landscape lenses are those which will, with a large aperture in the diaphragm, give a sharp

Fig. 37.

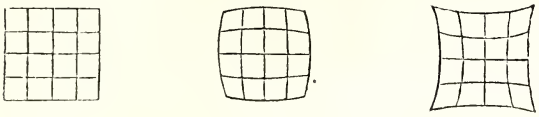


picture over a moderately large field; and with an aperture much reduced, extend that sharpness over an angle of eighty or ninety degrees on the base line.

It is now requisite we should speak of a defect inherent in the landscape lens which, although not affecting its use in the production of landscapes, militates against its utility in taking copies of anything requiring

absolute accuracy, such as maps and pictures, or in the delineation of architectural subjects. This defect is its inability to produce rectilinearity. As will have been ascertained from an inspection of fig. 35, the margin of a lens bends a ray to a somewhat greater extent than any other part of the area of such lens; and as, owing to the position of the diaphragm, the rays which come from the sides of the subject are transmitted by the margin of the lens, a certain amount of bending towards the centre results, it follows that a square building, a map, plan, or anything else that is to be reproduced, will not be represented precisely as it ought to be, but will experience a slight degree of curvature of the marginal lines. It is only in or towards the margin of the picture that such effect is noticed, but even though not readily observable to the eye, especially if the photographer has done his part well and with understanding, and has taken care not to force the lens to include a wide angle of the subject being copied, the application of a straight-edged rule will reveal the distortion of curvature, by which a square original becomes slightly barrel-shaped in the photograph, as shown in No. 2, fig. 38. The distortion here referred to is of quite a different nature

Fig. 38.



No. 1. No. 2. No. 3.

from another kind in which lines in a building which ought to be perpendicular in the picture are delineated with converging lines. This arises from another cause, and is altogether irrespective of the nature of the lens employed.

If the Lens, together with its mount, were entirely reversed, so that its convex surface should be pointed towards the view, the diaphragm being next the ground glass, the distortion would not be cured, but would as-

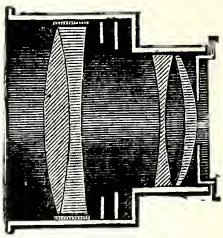
sume a precisely opposite character to what it did in the former instance. The distortion in that case was of a barrel shape; in this it is of the pincushion form, as shown in No. 3.

The entire elimination of all distortion is effected by having a lens on each side of the diaphragm, so that the barrel and pincushion curves neutralize each other, and meet together in one absolutely straight line, as in No. 1.

The optical condition for securing freedom from distortion consists in this, that every ray which falls upon an objective must emerge after transmission in a direction parallel to that at which it entered. Symmetry, whether mechanical or optical, in a combination, ensures this result, and we shall next come to speak of non-distorting combinations.

It will readily be perceived that under no circumstances could the condition described as that requisite

Fig. 39.



for rectilinear projection be obtained by the employment of any species of single lens, even if it were achromatized. Numerous forms of compound lenses have been devised to meet the requirements, and with one exception all of them have proved successful so far as concerns the giving of straight lines; that exception is the now little-used Orthoscopic or Orthographic combination, for which many claims were at one time made in support of the sentiment embodied in the name. But notwithstanding such claims, the fact that it did produce distortion could not long be gainsaid; but the curvature

of those marginal lines that ought to have been straight, was of a nature quite opposite to that produced by the Single Achromatic, an expansion rather than a contraction of the proportions in the drawing taking place, in proportion as it was distant from the centre. The combination (fig. 39) consists of a somewhat flat meniscus, achromatic at the outer end of a short mount, the convex side out; a smaller and negative achromatic being placed a little distance behind. This negative lens, which consists of a biconcave crown and a meniscus flint, corrects the aberration of the outside one, lengthens the focus and flattens the field.

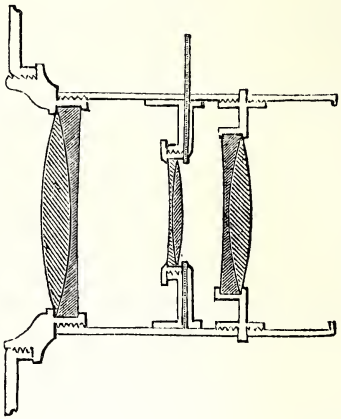
While failing for the specific purpose for which it was originally constructed, the Orthoscopic Lens, from its capability of working with a large aperture, answers admirably for out-door groups, or even portraits in a good light, and with very sensitive plates. It is also useful for producing an image of larger size than could be obtained by any other lens on a camera of a given length. The size of an image of any object in the negative depends upon the focus of the lens by which it has been taken. This focus is measured from, and determined by, the position of its optical centre; the optical centre of a well-constructed Single Achromatic landscape lens is rather nearer to the ground glass of the camera than the lens itself, but in the Orthoscopic combination it is outside of the lens entirely, so that with a given length of camera, a much larger image can, as we have stated, be obtained by this lens than by any other. This is a property of much value.

The "Triple Achromatic" (fig. 40) of Mr. J. H. Dallmeyer, was a decided improvement upon the Orthoscopic Lens, inasmuch as by it pictures quite free from distortion were obtained. This lens served a useful purpose in its day, but like the other it is now falling into disuse, having been supplanted by more effective and simpler combinations. It consists of a slightly meniscus achromatic, convex side out; a little distance behind this is a nearly plane meniscus concave achromatic, a larger lens

of the same form as that in the front being placed at the back end.

Apropos of the Triple Achromatic, Mr. Grubb has applied to single landscape lenses an additional front, composed of simple lenses of a form nearly similar to the two achromatics in Mr. Dallmeyer's combination—viz., plano-convex and plano-concave, the size of which, in connection with any achromatic landscape, cures its

Fig. 40.



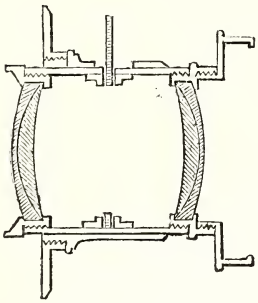
distortion, and renders it suitable for architectural purposes. Both of these lenses are formed of crown glass, and possess such curves as to make the two, when combined, in effect like a piece of plain glass, in the sense of their having no magnifying power. They are placed immediately in front of the diaphragm of the lens, the rounded surface of the plano-convex lens to the outside. This causes such a degree of displacement of the marginal rays as to cure distortion.

While on the subject of neutralizing the distortion of lenses which produce this bad quality, it may be said that the pincushion distortion of the Orthoscopic lens may be cured by a simple expedient devised by

the editor of this work. It consists in interposing a thick sheet of plate glass immediately in front of the sensitive plate, and as close to it as possible. The *rationale* of its action is this: a ray falling on its surface at a right angle is transmitted without being deflected, but in proportion to the obliquity of the incident ray so is it refracted in course of transmission, a fact quite apparent upon laying a thick slab of glass down upon printed matter and looking obliquely through it. The inward deflection caused by this oblique incidence balances the outward departure from rectilinearity caused by the form of the lens, the photographic result being freedom from distortion.

The death knell to the construction of several combination of lenses was struck when, almost simultaneously Steinheil, of Munich, and Dallmeyer, of London, introduced each a lens, which although possessing slight differences in construction are in effect

Fig. 41.



and general configuration so nearly allied as to be practically alike.

The Aplanat of Steinheil is constructed of two kinds of flint glass, a light and a dense kind, by which achromatism is effected in the same manner as by means of flint and crown. The rapid rectilinear of Dallmeyer is composed of flint and crown. The

diagram, fig. 41, explains the formation of both in a manner sufficiently plain to be understood. They work sharply with an aperture equalling about a seventh or eighth of the focus, and are thus well adapted for groups and portraits in a good light and with sensitive plates; while being symmetrical both in an optical and mechanical sense they give pictures free from distortion.

This class of lens, which is now very extensively manufactured, with certain slight modifications, is to be met with all over the world under various names, to produce which both the dead and the living languages have been placed under heavy contribution. When used with a small diaphragm it includes an angle of considerable extent, although, owing to the comparative flatness of the exterior surfaces, and the length of the tube in which the lenses are mounted, they can scarcely rank as wide-angle objectives. But even to this requirement they lend themselves with great degree of pliancy, for the editor has not unfrequently taken views which include an angle of ninety degrees by mounting a pair of these lenses tolerably close together, and inserting a diaphragm between them. Their internal curvature affords facilities for the transmission of a very oblique ray.

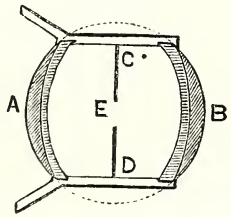
All the lenses constructed on the "rapid" principle, and according to the system shown in the last diagrams, must be formed of a peculiar kind of glass, possessing a greater degree of density than that of ordinary flint and crown. But an American optician, Mr. R. Morrison, has by means of an entirely different method of achromatizing, secured an angularity of aperture, and therefore a rapidity, equalling that of the rapid lenses mentioned by means of the flint and crown glass so long employed in other optical productions. The nature of this objective will be understood from the following description of one of ten inches in back focus, which was carefully examined. The exterior lens of either combination consists of a plano-

convex crown, the margin of which is in contact with a double concave flint. The radius of the former is 4 inches, that of each surface of the latter being 20·00 and 10·20 respectively, the flatter of the two surfaces being next to the plane surface of the crown-glass lens. The objective is symmetrical, both front and back combinations being alike. In other objectives by the same maker and of the same type, but more particularly in some exceeding twenty inches in focus, while both crown glasses are plano-convex, both combinations are otherwise dissimilar as regards curves. Owing to the flatness of the inner curves, this system favours to a greater extent than others the formation of large lenses at a moderate cost.

WIDE-ANGLE NON-DISTORTING LENSES.

In wide-angle lenses of the kind now to be considered it is essential that the meniscus form be very

Fig. 42.

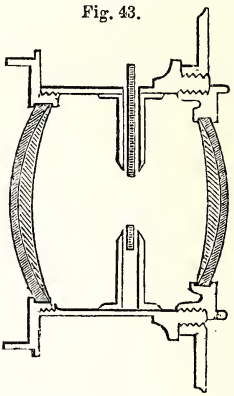


deep, so as to present a surface nearly at a right angle to the incident and emerging ray, whether it be an axial or oblique one. To meet this requirement the American globe lens was devised. In it the globular idea was carried out (*see* fig. 42) in its entirety, as the radius of the outer surface A B was measured from the centre E of the combination. It gave pictures free from distortion, and included a tolerably wide-angle, but often faulty from a flare spot in the centre, the result of a too close adherence to the globe form, for had the lenses been placed closer to C D, not only would a wider angle of

view have been included, but the conditions under which the flare spot referred to was produced would have been disturbed.

It is worthy of notice that Morrison's wide-angle lens, which is now extensively used in America, and gives pictures of a high degree of optical excellence, is erected upon what we may term the ruins of the globe lens. Its front consists of a deep meniscus achromatized in the manner of the globe, its back lens consisting of a simple non-achromatic crown meniscus, of a focus a little longer than its confrère. The diaphragm is placed between them in the ratio of their foci. Notwithstanding the non-achromatizing of the back lens, and the absence of any trace of over correc-

Fig. 43.



tion of the front, this combination has its visual and chemical focus practically coincident.

Both Dallmeyer and Steinheil have constructed wide angle lenses on the same principles as those which distinguish their rapid lenses already spoken of. But in the one case the Rapid was an outcome, in a sense, of the wide-angle rectilinear; while in the other, the rapid Aplanat was the precursor of the wide angle. The former is illustrated in the diagram (fig. 43).

The wide-angle Aplanat is small in diameter, and of a deeply curved form. Compared with their diameter, the lenses are very thick, and are mounted so closely together as not to allow much more space between them than suffices for the insertion of a diaphragm. Like its progenitor, it is formed of two kinds of flint-glass.

Those wide-angle lenses just described are typical of most others now being manufactured.

In the mounts of wide-angle landscape lenses, a great improvement has been effected by Messrs. Ross & Co., who have constructed quite a large series of symmetrical lenses of various foci, but all of which have the mount of the same diameter, and are thus capable of screwing into the same flange. This is a great convenience to the tourist or landscape artist.

PORTRAIT LENSES.

We now come to speak of that class of lenses which are more used than any other, that which, on account of its special qualities, is termed the Portrait Lens. The exceptional properties of this lens consist in its possessing a very large aperture or area of surface in comparison with its focus, this property being designated angular aperture.

Its aberrations are also corrected in a manner so perfect as to define with extreme sharpness, without a diaphragm; the practical result arising from such properties is that a sharp portrait can be taken in a very brief period of time and in a subdued light.

A lens possessing a large angular aperture is directly antithetical to a lens which includes a large angle of view. The latter embraces a wide extent of subject, but must be used with a small aperture; whereas the former embraces only a limited amount of subject, but works with a large aperture. Two lenses may be precisely similar, so far as regards diameter, but if one be of shorter focus than the other, its angular aperture will be greater. This property confers the great advantage of rapidity of action. A lens only one inch n diameter may work more rapidly than one of four

inches, because of its focus in relation to its aperture being shorter and admitting a ray of greater intensity.

By the skill of the opticians, lenses are now constructed having an aperture so great as to equal twice their foci. Such lenses are only of limited utility when worked without a diaphragm, for they cover only a small portion of the plate sharply, while their depth of defining power has only little range; but owing to the flood of light transmitted, they work with an extreme degree of rapidity and are invaluable in the taking of portraits of children or paralytic persons. But both the field of delineation and the depth of definition may be extended by the insertion of a diaphragm, these advantages being obtained at the expense of illumination and consequently of increased exposure.

In the construction of a portrait objective it is necessary that the front lens be an achromatic of plano-convex form, or nearly so, and that its convex side be next to the object to be taken. Used alone in this way it would produce a tolerably sharp and bright image without any diaphragm, but such sharpness would be confined to a limited area in the centre of the picture. A second, or back lens, is therefore made to work in conjunction with the front one for the twofold purpose of securing a distribution of sharp definition over a larger field, and incidentally, by shortening the focus, adding materially to rapidity of action.

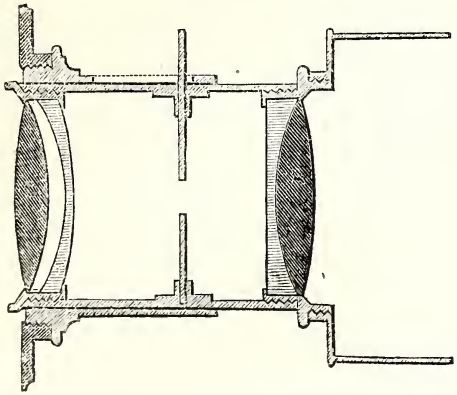
The aberrations of the front lens, especially for oblique rays, are such as to render it altogether impossible that these can be transmitted to a focus, especially on the same plane as that to which the axial rays converge, hence the back lens must consist of a combination of two simple lenses, the materials and curvatures of which are so adjusted as not only to form an achromatic in itself, but to possess so great an amount of negative spherical aberration as shall neutralize the positive aberration of the front lens and exercise so much control over the oblique pencils as not only to bring them all to a focus, but also to lengthen them out to such an extent as to cause that focus to fall upon the same plane

as the central rays, and thus yield that great boon to the portraitist, a sharp flat field.

A back lens, or, more correctly, a pair of lenses, of a portrait combination, cannot when used alone give a sharp image, owing to its negative aberration, by which its margin is of a longer focus than its centre.

The discovery of this balancing of the aberrations, and consequent production of a portrait combination, is due to Professor Petzval, the eminent mathematician of Vienna, and the figure (44) shows the portrait lens in the form in which it was invented by him, and is manufactured at the present day.

Fig. 44

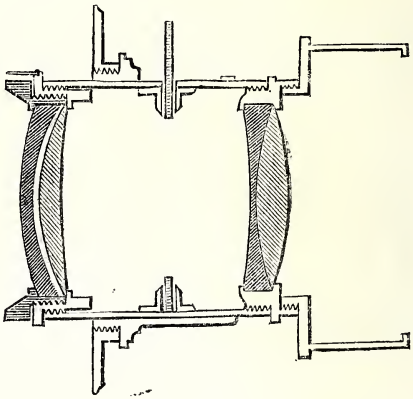


This portrait objective is only suitable under certain circumstances for views or out-of-door pictures; these are, its being worked with full aperture, and the shielding from it of all extraneous light, especially that from a bright sky. By making use of a small diaphragm, although all the depth and sharpness over a larger field arising from a diaphragm is secured, yet will there be a troublesome flare or light spot in the centre of the picture, that will spoil the appearance of the picture. This is not observed when the lens is worked with its open aperture. When used for copying pictures, or other work *inside* of the studio, the

flare spot is not produced, no matter how small may be the aperture in the diaphragm.

There is another way, different from that described, by which the posterior combination of a portrait objective may be constructed. It was first applied by Mr. Dallmeyer, and in it both the form and relative positions of the elementary glasses are changed. A meniscus crown is placed close to, although not in contact with a concavo-convex flint lens, the exterior form of the two being slightly meniscus. The cut shows the nature of this combination.

Fig. 45.



The two inner or contiguous surfaces of the back pair cannot be placed in optical contact by means of transparent cement in the same way as the front ones, owing to a dissimilarity of curvatures, by which is obtained the requisite amount of negative spherical aberration to flatten the field. When the back elements are placed as close together as possible, the objective defines sharply; but by unscrewing them so as to effect ever so slight a degree of separation, then does the sharp and crisp definition give way to definition of a lower order which is useful for many purposes.

CHAPTER XXIII.

ON BINOCULAR VISION AND THE STEREOSCOPE.

An object is said to be "stereoscopic" (στερεος, solid, and σκοπεω, I see) when it stands out in relief, and gives to the eye the impression of solidity.

This subject was first explained by Professor Wheatstone in a memoir on binocular vision, published in the "Philosophical Transactions" for 1838; in which he shows that solid bodies project different perspective figures upon each retina, and that the illusion of solidity may be artificially produced by means of the "Stereoscope."

The phenomena of binocular vision may be simply stated as follows:—If a cube, or a small box of an oblong form, be placed at a short distance in front of the observer, and viewed attentively with the right and left eye separately and in succession, it will be found that the figure perceived in the two cases is different; that each eye sees more of one side of the box, and less of the other; and that in neither instance is the effect exactly the same as that given by the two employed conjointly.

A silver pencil-case, or a pen-holder, may be used to illustrate the same fact. It should be held at about six or eight inches distant from the root of the nose, and quite at right angles to the face, so that the length of the pencil is concealed by the point. Then, whilst it remains fixed in this position, the left and right eye are to be alternately closed: in each case a portion of the opposite side of the pencil will be rendered visible.

The diagrams on the next page exhibit the appearance of a bust as seen by each eye successively.

Observe that figure 47, which represents the impression received by the right eye, is more of a full face than figure 46, which, being viewed from a point removed a little to the left, partakes of the character of a profile.

The human eyes are placed about $2\frac{1}{2}$ inches, or from that to $2\frac{5}{8}$ inches, asunder; hence it follows that, the points of sight being separated, a *dissimilar* image of a

Fig. 46. Fig. 47.



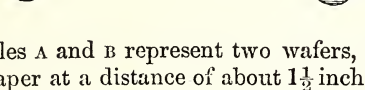
solid object is formed on the retina of each eye. We do not however see *two* images, but a single one, which is stereoscopic.

In looking at a picture painted on a flat surface the case is different; each of the eyes, as before, receives an image, but these images are in every respect similar; consequently the impression of solidity is wanting. A single picture, therefore, cannot be made to appear stereoscopic. To convey the illusion, *two* pictures must be employed, the one being a right and the other a left perspective projection of the object. The pictures must also be so arranged, that each is presented to its own eye, and that the two appear to proceed from the same spot.

The reflecting stereoscope, employed to effect this, forms *luminous images* of the binocular pictures, and throws these images together, so that, on looking into

the instrument, only a single image is seen, in a central position. It should, however, be understood, that no optical arrangement of any kind is indispensably required, since it it quite possible, with a little effort, to combine the two images by the unaided organs of vision. The following diagram (fig. 48) will make this obvious :—

Fig. 48.



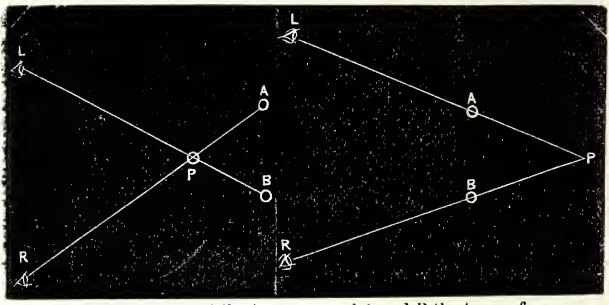
The circles A and B represent two wafers, which are stuck on paper at a distance of about $1\frac{1}{2}$ inch from each other. They are then viewed, either by squinting strongly, until the right eye looks at the left wafer and the left eye at the right wafer, or else by focussing the eyes for a distance beyond the wafers, which is easily effected by looking at a point midway between, but giving the attention to the indistinct wafers on each side, until the right eye at length looks at the right and the left eye at the left wafer ; in both cases the two wafers at first appear double, four images being seen, of which two gradually approach until they coalesce, and the resulting image appears in the first case *in front*, and in the latter case *behind* the paper. The mode in which coalescence is effected in both cases may be thus explained.

The perception of a *single* object, while using *two* eyes in ordinary vision, is due to the eyes being directed to the object in such a manner that the picture formed in each eye falls on similar parts of the retina. If, while viewing an object, one of the eyes be pressed by the finger, the object becomes double, from the position on the two retinæ not corresponding. From the same cause, on first trying to fix the two eyes on the two wafers, they appear double until the *optic axis* of each eye (or a line of indefinite length drawn through the centre of the pupil from the central and most distinctly

seeing part of the retina) is directed fully to each wafer. When this is the case, a similar picture falls on similar parts of each, and the two objects are perceived by the mind as one. The other less distinct images, one on each side of the principal one, are due to each eye perceiving its neighbour's wafer, but on points of the eyes that do not correspond.

The cause of the combined image standing out in front or behind the paper is due to *the mind always referring the place of an object to the point where the optic axes meet*, and when the two wafers are united by squinting, this point is *in front*, and when by distant focussing, *behind* the paper. This will be evident from the following diagrams :—

Fig. 49. Fig. 50.



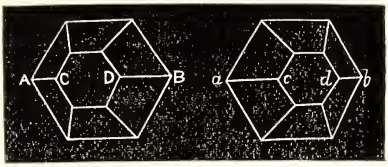
R and L represent the two eyes, and A and B the two wafers.

Fig. 49 represents union by squinting; the optic axis of each eye is directed to the opposite wafer, and the image is referred by the mind to P in front, where the axes cross. Fig. 50 *shows the ordinary way of viewing with the Stereoscope*, where each eye is directed to its own wafer. Here the optic axes meet beyond the wafers at P, and the compound image is perceived in the same place.

If, instead of two similar objects as wafers, the right and left perspective views of an object, such as the following of an hollow hexagonal cone, are viewed in a

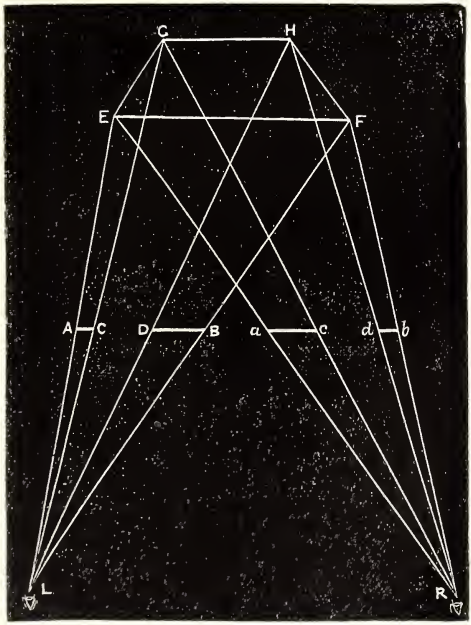
similar manner, a sensation of depth and elevation is obtained as soon as the images coalesce, the different

Fig. 51.



parts of the cone appear at different distances from the observer, and, what is more singular, the appearances are reversed by the two modes of causing the pictures

Fig. 52.

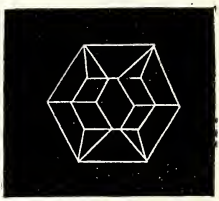


to coalesce. The diagram, fig. 51, viewed by focussing the eye for a distance, or by the Stereoscope, repre-

sents a cone, with the small hexagon distant; but by squinting, the small end is made to stand out towards the observer. As the former is always the way of viewing objects by the Stereoscope, it is only necessary here to explain how the sensation of depth and distance is produced by distant focussing, or viewing each half with the eye of the same side, and for the sake of simplicity only four points in each figure, A, C, D, B, and *a*, *c*, *d*, *b*, need be taken for the purpose of illustrating the mode in which the eye has to unite every corresponding pair of points in turn. In the diagram, fig. 52, these letters represent the same points of the hexagons, as in fig. 51.

The points A and *a*, which correspond in the two larger hexagons, are united when the right optic axis

Fig. 53.

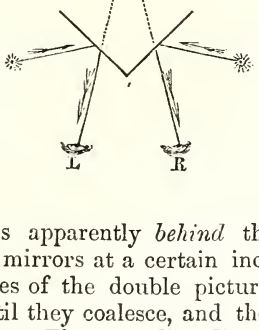


R *a* is directed to *a*, and the left L A to A; but the resulting single point *appears to be* at E, where these axes meet: so, in like manner, B and *b* unite, and form one point, apparently, at F. The points C *c* of the smaller hexagons being more distant from each other than A from *a*, or B from *b*, can only be united by *a more distant* prolongation of the optic axes L *c* and R *c* to the point of union G, which thus appears to be the position of these points of the smaller hexagons, and so with regard to D and *d*; and as these points are merely taken as samples of the whole, the result is that the corresponding parts of the lesser hexagons being more distant from each other than those of the greater hexagons, the former, when united, appear more distant than the latter, and the figure *stands out* from the paper.

The Stereoscope is merely an instrument to cause a superposition of the right and left views; but this alone is not sufficient to produce a stereoscopic effect, as the diagram, fig. 53, will show, in which the two halves of fig. 51 are represented superposed, the two outer hexagons coincide, but the similar parts of the two inner need still to be brought into union in the manner represented in fig. 52, and the various distances at which the optic axes meet appear to the mind to be the distance of the objects represented.

In Mr. Wheatstone's reflecting Stereoscope, *mirrors* are used. The principle of the instrument is as follows:—Objects placed in front of a mirror have their

Fig. 54.



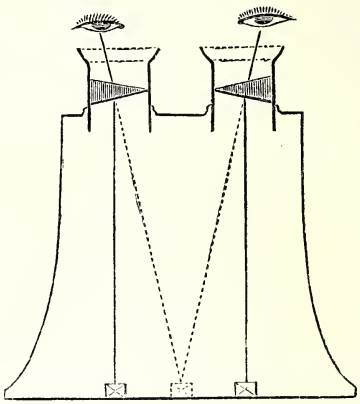
reflected images apparently *behind* the mirror. By arranging two mirrors at a certain inclination to each other, the images of the double picture may be made to approach until they coalesce, and the eye perceives a single one only. The preceding diagram will explain this.

The rays proceeding from the star on either side pass in the direction of the arrows, being thrown off from the mirror (represented by the thick black line) and entering the eyes at R and L. The reflected images appear to the mind behind the mirror, uniting at the point A, where the optic axes meet.

The reflecting Stereoscope is adapted principally for viewing large pictures. It is a very perfect instrument, and admits of a variety of adjustments, by which the apparent size and distance of the Stereoscopic image may be varied almost at pleasure.

The refracting Stereoscope is a more portable form of apparatus. A sectional view of the common form is given in the diagram (fig. 55).

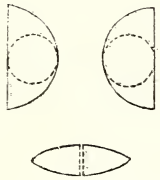
Fig. 55.



The brass tubes to which the eyes of the observer are applied contain each a semi-lens, formed by dividing a common lens through the centre and cutting each half into a circular form (fig. 56). The half-lens viewed in section (fig. 56) is therefore of a prismatic shape, and when placed with its sharp edge as in the diagram (fig. 55), alters the direction of the rays of light proceeding from the picture, bending them outwards or away from the centre, so that, in accordance with the law previously mentioned, the mind refers them to the direction of the prolonged optic axes—represented for one pair of points by dotted lines (fig. 55), and the corresponding parts appear to be at the various distances,

at which the optic axes, directed to them, meet. In the instrument as it is often sold, one of the lenses is made movable, and by turning it round with the finger and thumb it will be seen that the positions of the images may be shifted at pleasure.

Fig. 56.



Stereoscopes are now often mounted with whole lenses in place of the semi-lenses above described. In that case the images coalesce by an involuntary action of the eyes of the observer. If indeed the whole lenses were set wider apart than $2\frac{1}{2}$ inches, it might be conjectured that vision would take place principally through the inside edges, and that the same effect as that of a semi-lens would be produced. A single experiment, however, will suffice to show that even when the centres of the lenses are exactly opposite to the eyes, the two pictures combine without any effort.

Rules for taking Binocular Photographs.—In viewing very distant objects with the eyes, the images formed on the retinæ are not sufficiently dissimilar to produce a very Stereoscopic effect; hence it is often required, in taking binocular pictures, to separate the Cameras more widely than the two eyes are separated, in order to give a sufficient appearance of relief. Mr. Wheatstone's original directions were, to allow about one foot of separation for each twenty-five feet of distance; but considerable latitude may be permitted.

If the Cameras are not placed far enough apart, the dimensions of the stereoscopic image from before backwards will be too small,—statues looking like bas-

reliefs, and the circular trunks of trees appearing oval, with the long diameter transverse. On the other hand, when the separation is too wide, the reverse obtains—objects for instance which are square, assuming an oblong shape pointing towards the observer.

To understand the cause of this, it is necessary to refer to fig. 52, where it was shown that those corresponding parts in the two halves of a stereoscopic picture which are most widely separated, appear most distant when united in the Stereoscope, and hence the greater the separation, the greater is the apparent distance of the object; but the effect of separating the Cameras too widely is to produce too great separation of the distant parts of an object, as a little reflection on fig. 51 will show; it is evident that if the eyes, or the Cameras which represent them, were separated further in viewing the hollow cone, more of the sides D B and *a c* would be seen, and consequently the smaller hexagons would be placed more apart, and so when the two images were united in the Stereoscope, the cone would appear longer.

The effect is most observable when the picture embraces a variety of objects, situated in different planes. In the case of views which are quite distant, no near objects being admitted, the Cameras may be placed with especial reference to them, even as far as twelve feet apart, without producing distortion.

It is sometimes observable, in looking at Stereoscopic pictures, that they convey an erroneous impression of the real size and distance of the object. For instance, in using the large reflecting Stereoscope, if, when the adjustments have been made and the images properly united, the two pictures be moved slowly forward, the eyes remaining fixed upon the mirrors, the Stereoscopic image will gradually change its character, the various objects it embraces appearing to become diminished in size, and approaching nearer to the observer; whilst if the pictures be pushed *backwards*,

the image will enlarge and recede to a distance. So, again, if an ordinary slide for the lenticular Stereoscope be divided in the centre, and—looking into the instrument until the images coalesce—the two halves be slowly separated from each other, the solid picture will seem to become larger and to recede from the eye.

It is easy to understand the cause of this. When the pictures in the reflecting Stereoscope are moved *forwards*, the convergence of the optic axes is increased: the image therefore appears *nearer*, in accordance with the last-mentioned law. But to convey the impression of proximity to an object is equivalent to an apparent diminution in its size, for we judge of the dimensions of a body very much in relation to its supposed distance. Of two figures in bronze or marble, for instance, appearing of the same height, one known to be a hundred yards off might be considered colossal, while the other, obviously near at hand, would be viewed as a statuette.

The most convenient camera for stereoscopic pictures is one for a plate 8 by 5 inches. It must be fitted with a pair of precisely similar lenses, either portrait or landscape objectives, according to the nature of the subject. The camera must have a partition to confine the rays from each lens to its own division. This is equivalent to two cameras placed side by side. The lenses may be mounted about $3\frac{1}{2}$ inches apart.

CHAPTER XXIV.

CHROMOTYPE OR LAMBERTYPE.

In the article on Carbon Printing in another page of this book, we have described that process, with several improvements that have been effected since the principles involved in it have been carried out to a state of practical perfection. We have now to describe a carbon process of another kind, which, although not sensibly different from the other in its principles of action, is yet carried out in practice so differently in regard to its minutiæ, and refined as respects results, as to warrant its being considered as revolutionary. We allude to the Chromotype, or, as it is termed by some, the Lambertype process.

In this process, the picture instead of being developed upon a hard and unyielding surface, such as that of a zinc plate, is supported upon a film of somewhat porous collodion. This film is afterwards transferred with the print (and may be said to form part of the picture itself), the glass supporting it having previously been prepared to facilitate its removal. The advantage gained by the employment of the collodion is twofold. It tends to hold together the more delicate portions of the picture during the development, and, by reason of the gloss conferred by the film, it gives great transparency to the shadows, and thereby overcomes one of the hitherto weak points in the carbon process—namely, that the pictures are heavy, and lack the brilliancy of those made in silver, which is the case when zinc plates or flexible support are used. Until the introduction of this modification, the carbon process could not be considered as one well adapted for the pro-

duction of small work—such as the carte and cabinet size; hence its application was principally confined to pictures of large dimensions. With this modification however we have the means of producing prints possessing either the surface of ordinary, or of doubly albuminized paper, or one equal to that of the so-called enamelled prints, now so much in vogue—and possessing equal transparency in the shadows. For the Chromotype process a special tissue is supplied, but its speciality consists in its colour only—that of a rich purple-toned silver print. In its composition, it does not differ from the ordinary portrait tissues, any of which will answer the purpose quite as well, so far as the process itself is concerned. With this explanation we will proceed to the details of the manipulation.

Sensitizing the Tissue.—The strength of the bath should be governed by the temperature, as well as by the general character of the negatives to be printed from. The higher the temperature, the weaker should be the solution, and *vice versâ*. It may be as well to mention here, that the stronger the bath is, the softer will be the resulting prints, and the weaker it is, the greater will be the contrasts; hence, for negatives of a weak and delicate character a dilute bath should be employed, and for more vigorous or hard ones, a more concentrated solution must be used in order to obtain the best results from them. A very suitable bath for general purposes is—

Bichromate of potash	4 oz.
Water	100 oz.
Liquor Ammonia	1 dram.

For use in summer, or for negatives lacking in contrasts, the proportion of water should be increased to 120 ounces. In winter, or for negatives with extra vigour, it will be advisable to reduce the water to 80 ounces. The temperature of the bath should never exceed 50° in summer, or there will be a danger of the pigmented coating

dissolving and running off the paper when it is suspended to dry in a heated atmosphere. Sufficient of the solution should be poured into a porcelain dish or zinc tray (the latter is usually employed), so as to be at least $1\frac{1}{2}$ inches in depth. The tissue, cut to convenient sizes, is now immersed, and any adherent air bubbles quickly removed with a broad, flat, camel's-hair brush. It should be kept in motion all the time it is in the solution, in order to secure uniformity in sensitiveness throughout the sheet. With regard to the time of immersion, no definite rule can be laid down, as so much must depend upon the temperature, for if it be very cold the solution will be absorbed by the gelatine much slower than if it were warmer. The best guide for removal is when the tissue has become thoroughly pliable. The longer the tissue is allowed to remain in the solution the greater will be the quantity absorbed, and the more sensitive it will become; hence it will be seen that, with the same solution, it is quite possible to obtain various degrees of sensitiveness, so as to suit different characters of negatives. The more sensitive the tissue is made, the shorter the time it will keep in good working condition.

When the tissue is deemed sufficiently sensitized it is slowly drawn out, face downward, over the edge of the dish—or better still, over a glass rod fixed upon it. This will remove a large proportion of the superfluous solution. It is now laid, face upward, on a sheet of stout blotting board, which is then placed across a line or rail to dry. A better plan than this, more particularly when the temperature is high, is, after removing the tissue from the solution, to place it, face downward, on a plate of glass, and then to pass a squeegee lightly over the back; by this means a greater quantity of the superfluous solution is removed, and consequently there will be less risk of the coating running off in hot weather. Also, the tissue will dry more easily—a great advantage in damp weather; and, furthermore,

its surfaces will be more smooth and even, so that better contact with the negative can be secured in the printing. The sensitizing may be conducted in an ordinary room, as the tissue is *practically* insensible to white light while wet, and only acquires sensitiveness as it dries.

The Drying of the Tissue.—This is a somewhat important part of the process; indeed, it has been asserted by some, that if the tissue be properly dried, half the difficulties pertaining to carbon printing have been surmounted. At one period it was supposed that the tissue could not be dried too quickly, as by that means the greatest degree of solubility was secured. Further experience, however, has proved this to be a fallacy, and that excessive solubility is by no means desirable—and for the following reasons—viz.:—It is liable to cause reticulation, when the prints are developed on a collodion film; the delicate half-tints cannot be so well preserved; and the tissue will prove very insensitive. On the contrary, if the time of drying be too protracted, then the tissue will be more or less insoluble, and the unacted upon portions of gelatine can only be dissolved with difficulty in the development. Also, it will be very sensitive, and quickly become totally insoluble by keeping. The best conditions of drying may generally be secured by suspending the tissue in a room where a fire has been burning for some hours and then allowed to die out. If sensitized over night, it should be quite dry by the morning. As a rule, carbon tissue that has occupied from six to nine hours in drying will usually be found in the best working condition. When dry, it should be carefully preserved from the influence of the atmosphere in a metal case. It will then keep in good working order for many days. The author has kept it, under exceptionally favourable circumstances, for several weeks without deterioration. The time of exposure in printing is judged in the same manner as described in the chapter on carbon printing. Chromotypes, when mounted with the highest gloss, are usually

printed with an ornamental border, bearing an imprint of the name of the artist, &c. This is accomplished by double printing. There are several ingenious contrivances for enabling accurate registration to be secured, but it would manifestly be out of place to describe them in a work of this character.

After the pictures are printed, they should be developed as soon as convenient, or there will be a risk of their becoming darker, as the action of light, once started, progresses even when the prints are kept in darkness. This property in the carbon process is termed the "Continuating action of light," and is materially accelerated if the prints be kept in a moist and warm atmosphere—and practically arrested if they be made thoroughly dry, and preserved in a cool place. Carbon printers take great advantage of this property for securing a larger number of prints in a given time—for by printing only half, or even to a third of the requisite depth, and keeping them in the dark for from twelve to twenty-four hours, according to the state of the atmosphere, "fully exposed" impressions can be secured.

Development of the Prints.—In the first place, some glass plates are required, of a convenient size for the work in hand. It is customary to develop several prints on the same plate, instead of having separate plates for each print. A glass 15 inches by 12 is well suited for five cabinet-size pictures, when printed with the masked border. Beginners in the Chromotype process are usually advised to employ opal glass, of the kind known as "patent plate opal"—as, by reason of its white surface, the development can be more easily judged than when transparent glass is used. Beyond this, the opal glass offers no advantage over the ordinary, and it is very expensive, its surface is easily scratched, and all scratches on the glass will be apparent in the finished picture. Whichever kind of glass be employed, the treatment is the same—its surface must be prepared to enable the collodion film carrying the picture

to be afterwards transferred. There are two methods of accomplishing this. One is to rub the surface over with powdered talc, the other is to give the glass a slight coating of wax. Both methods have their advocates, but the writer prefers the latter, notwithstanding that it involves a little more trouble.

The waxing solution is made by adding 1½ drams of pure yellow bees-wax to a pint of benzol. This should be allowed to digest for a day or two with occasional agitation; it is then allowed to subside, afterwards the clear portion is decanted for use. A little of this solution is poured on to the plate, and evenly distributed with a piece of soft rag, or a pledget of "papier Joseph." After the benzol has evaporated, the glass is carefully polished with a piece of soft flannel, until all streaks are removed, and its surface appears clean and brilliant. The plate is then coated with collodion, of good body, made with pyroxylin of a somewhat porous character—about 5 or 6 grains to each ounce of solvent is a good proportion to employ. After the collodion has been allowed to set, rather more than is customary in the negative process, the plate is plunged into clean cold water and the ether and alcohol thoroughly washed out; the plate is then ready for immediate use, or, it may be kept in the water until required.

To Mount the Prints for Development.—Place the collodionized glass on a smooth flat board, and immerse a sufficient number of prints to cover its surface in a dish of clean cold water. Remove all air bells, and allow the prints to remain until they become quite limp, but not long enough for them to curl up gelatine side *outward*. Now flood the plate with water, and place them in position upon it. When all are arranged, a piece of india-rubber cloth, somewhat larger than the glass, is laid, rubber side outward, over them, and a squeegee applied as described in the chapter on carbon printing. The cloth is now removed, and the glass, with the adherent prints upon it, is placed between sheets of blotting paper for from five

to ten minutes. The object of the india-rubber cloth is to prevent the collodion film from being abraded with the squeegee, and afterwards washing up during the development. The plate is now placed in water at a temperature of 90°. After the lapse of a minute or two, the colouring matter will be seen to exude from the edges of the prints. When this occurs one corner is carefully raised, so as not to injure the collodion, and the paper lifted off. The development of the prints is then conducted as described in the chapter on carbon printing. Should it be found that the pictures are over-printed, the temperature of the water may be increased somewhat. If, on the contrary, they should show signs of under-exposure, the development must be completed with cooler water. By varying the temperature of the developing water any error in the exposure, within reasonable limits, may be compensated for.

When the development is completed, the plate is well rinsed with cold water, and then plunged into a solution of alum — 5 ounces in a gallon of water—where it is allowed to remain for about five minutes. It is then well rinsed under the tap, and reared up to dry in a place free from dust. The action of the alum is to render the gelatine, which up to this time is partially soluble, insoluble, so that it can no longer be dissolved with hot water—the film in fact being practically converted into leather.

If the prints are to be mounted with the full gloss—the "enamelled" surface—the spotting must be done before the transfer paper is applied. For this purpose, oil colours thinned with spirit of turpentine are used; they will be dry in an hour or so after they are applied. The effect of the pictures may sometimes be enhanced by strengthening the shadows, or softening the lights, with powder colours applied with a wash-leather stump.

To Transfer the Prints.—A sheet of double transfer paper, by preference of a slightly blue shade, a trifle

smaller than the glass plate, is placed in warm water (100°) until its prepared surface acquires a "slimy" condition. It is then removed and laid on the prints, which have previously been wetted with water, and the squeegee brought into use so as to expel all air bubbles and as much of the water as possible. The plate is then placed between blotting paper for a short time, to absorb the superfluous moisture. If the prints are required with the surface of doubly albuminized paper the prints are allowed to dry; they are then stripped off and mounted with starch paste, and then rolled in the ordinary manner. If less gloss still be required, the prints, after stripping, are placed between sheets of damp blotting paper for an hour or so, and then mounted while they are still moist.

But if the highest possible gloss be desired, the mounts must be attached before the prints are removed from the glass, which is done in the following manner. When the back of the transfer paper has become surface dry, and no more, the plate is held up to the light, and the opposite (diagonally) corners of each print is marked with a pencil. These marks are to serve as a guide for adjusting the mounts in the proper position. When all are marked, the back of the transfer paper is coated with thick starch paste, applied with a sponge, or thin glue; the Writer prefers the latter. The cards, which have previously been damped, are also coated with the cement, and then placed in position. When all are arranged, the plate is put under pressure between blotting paper for an hour or two, and then reared up to dry. In order to prevent the prints springing off the glass before they are quite dry, which would cause an inequality in the gloss, American clips should be put round the edges.

When the prints are perfectly dry, and not before, they are stripped off, and afterwards trimmed round the edges with a pair of sharp scissors. In place of mounting the prints on separate cards, it is customary with many to employ one sheet of cardboard

the same size as the glass, and to cut it up afterwards. Sometimes, instead of mounting the prints direct on to the mounts, a second or a third sheet of transfer paper is applied, and when the whole is dry the prints are stripped off and trimmed; they are then mounted on the cards. By this means considerable trouble is saved, as it is much easier to apply an extra sheet or two of transfer paper than the cardboard mounts, and the additional thickness of paper prevents the mounting material from injuring the gloss of the picture.

APPENDIX.

HOW TO ASCERTAIN THE EQUIVALENT FOCUS OF A LENS.

By the "equivalent focus" is meant that measured from the optical centre of the combination, and which yields an image of a size corresponding with that obtained by using a thin simple lens. The knowledge of this is requisite for copying, enlarging, and other purposes.

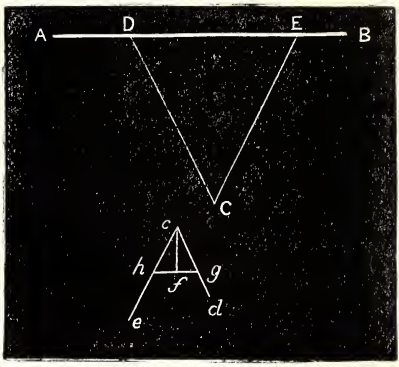
An easy, although not *absolutely* accurate, method consists in focussing an engraving, or other well-defined object, as sharply as possible, having previously adjusted its distance from the camera so that the image on the ground-glass shall be of precisely similar dimensions to the original. Measure the distance between the ground-glass and the printed matter, and one-fourth of that measurement is the equivalent focus of the lens.

By some the equivalent focus is measured from midway between the lenses in the case of portrait and symmetrical combinations, or from the curved surface of a single achromatic landscape lens; but such measurements will yield results which are only approximatively accurate. The method first described by the late Mr. Thomas Grubb is one by which perfect accuracy may be obtained. Place the camera upon a level table on a sheet of paper fastened down upon the latter; then, having ascertained by inspection the limits of the subject delineated upon the focussing-screen, turn the camera round until the object at one extreme occupies the centre of the ground-glass, and accurately coincides with a

pencil line made thereon. Now, with a pencil draw a line on the paper beneath the camera, parallel with one side of the latter; turn the camera round until the object at the other extremity of the subject coincides with the pencil line on the focussing-screen, and draw another line on the paper as before. The angle formed by the two lines thus drawn will show the "angle of picture" included. But this is not all; for if we draw a line *opposite to the angle* thus found, at such a distance therefrom as shall allow the third line, bounded by the two previous ones, to be of the same length as the focussing-screen, a perpendicular let fall from the angle upon the third line will give the *equivalent* focal length of the lens employed. This equivalent focal distance may or may not agree with the distance of the screen from the lens—most probably *not*, especially if it be a double combination.'

To simplify this matter, we append the following diagram :—

Fig. 57.



Let A B represent a moderately distant view, and C the place of the camera. On focussing, we find the portion included on the ground-glass to be from D to E only; this is the angle of picture. If we now turn the camera towards D, so as to make its image fall on a line in the centre of the focussing-screen, and draw a line parallel with the side of the camera, we shall have a line parallel to C D—viz. *c d*. On

turning the camera towards E, and making its image fall on the same mark on the screen, another line drawn parallel with the same side of the camera will also be parallel with C E—viz. *c e*, and these two lines are inclined to one another exactly in the same ratio as are C D and C E.

By measurement upon the ground-glass, we find the distance between the images of the objects D and E to be equal to *g h*; and if we now place this line exactly opposite the angle *c*, so as to be bounded by the lines *c d*, *c e*, and let fall the perpendicular *c f*, the distance *c f* is the *equivalent* focus of the lens. Any one possessing a lens and camera need therefore be under no uncertainty about the *equivalent focus* of the former; and this once ascertained, he can always calculate the angle of any view he may take with it, no matter upon what sized plate he may operate.

QUANTITATIVE TESTING OF SOLUTIONS OF NITRATE OF SILVER.

The amount of Nitrate of Silver contained in solutions of that salt may be estimated with sufficient delicacy for ordinary Photographic operations by the following simple process :—

Take the *pure* crystallized Chloride of Sodium,—which operative chemists make purposely for analysis by dissolving the best Carbonate of Soda in pure Hydrochloric Acid,—and either dry it strongly or fuse it at a moderate heat, in order to drive off any water which may be retained between the interstices of the crystals; then dissolve in distilled water, in the proportion of $8\frac{1}{2}$ grains to 6 fluid ounces.

In this way, a standard solution of salt is formed, each drachm of which (containing slightly more than one-sixth of a grain of salt) will precipitate half a grain of Nitrate of Silver.

To use it, measure out accurately one drachm of the Bath in a minim measure, and place it in a two-ounce stoppered phial, taking care to rinse out the measure with a drachm of distilled water, and to add the rinsings to the fluid drachm of Bath; then pour in the salt solution, in the proportion of a drachm for every 4 grains of Nitrate *known to have been present*, in an ounce of the Bath which is to be tested; shake the contents of the bottle briskly, until the white curds have

perfectly separated, and the supernatant liquid is clear and colourless; then add fresh portions of the standard solution of salt by 30 minims at a time, with constant shaking. When the last addition causes no *milkiness*, read off the total number of drachms employed (the last half-drachm being subtracted), and multiply that number by 4 for the weight in grains of the Nitrate of Silver present in an ounce of the Bath.

In this manner the strength of the Bath will be indicated within two grains to the ounce, or even to a single grain if the last additions of standard salt-solution be made in portions of 15 instead of 30 minims.

Supposing the Bath to be tested is thought to contain about 28 grains of Nitrate to the ounce, it will be convenient to begin by adding to the measured drachm 6 drachms of the standard solution; afterwards, as the milkiness and precipitation become less marked, the process must be carried on more cautiously, and the bottle shaken violently for several minutes, in order to obtain a clear solution. A few drops of Nitric Acid added to the Nitrate of Silver facilitate the deposition of the Chloride; but care must be taken that the sample of Nitric Acid employed is pure and free from Chlorine, the presence of which would cause an error. The delicacy of this mode of testing may be increased by adding to the Silver solution a little Bichromate of Potash, omitting the Nitric Acid; a deep red precipitate of Chromate of Silver is thus formed, which tinges the Chloride of Silver, formed on adding the standard solution, until the last, when all the Silver having been precipitated, the Chloride of Sodium finally decomposes the red Chromate of Silver into the white Chloride, and the completion of the operation is evident from the change of colour in the precipitate.

The Photographer may perhaps require to perform these operations when pure Chloride of Sodium is not immediately obtainable. In that case the ordinary commercial Chloride of Ammonium may be substituted, $7\frac{3}{4}$ grains being dissolved in 6 fluid ounces of water. It is advisable however, when using a Chloride of doubtful purity, to take the precaution of trying the strength of the standard saline solution, by testing it upon 30 grains of pure dried Nitrate of Silver dissolved in an ounce of water.

SAVING OF SILVER AND GOLD FROM WASTE SOLUTIONS AND RESIDUES.

The judicious collection of wastes from solutions of the noble metals is one of the best economies that a photographer can practise. Seeing that these substances are most expensive items which must be largely used, and also bearing in mind the fact that very little of them is really used up in forming the Photographic image, it stands to reason that the rest can be recovered.

1st. A large glazed earthenware or porcelain jar is provided; or an ordinary cask, tarred and dried inside, will answer. It should be fitted with a tap near the middle, to draw off superfluous water when required. Into this jar are thrown all the drippings of Nitrate of Silver from sensitized paper, the first washing water of vessels which have contained the Nitrate, the first washing water of Photographic prints *before* toning, and in short all *waste* silver salts that can be made insoluble by a Chloride or other Haloid.

The jar should be well supplied with Chloride of Sodium (common salt) to reduce the Silver to Chloride. But sometimes it happens that the latter insoluble compound is in a state of such fine division that it does not readily subside so as to enable one to draw off, without waste, part of the superfluous liquid when necessary. In that case, acidulate with a little Hydrochloric or Sulphuric acid, and stir the whole well up. In a short time the supernatant liquid will be quite clear and free from silver.

2nd. Another saving of Silver arises from the filters, the clippings of prints, and the bits of blotting-paper used for absorbing waste drops either in the Negative or Positive processes. These should all be dried and placed in a bag until they accumulate in sufficient quantity for reduction. To effect this the papers or other absorbents of Nitrate of Silver are burnt and the ashes carefully preserved. The burning may be done in an ordinary grate. First clear out all the ashes from the fireplace, fill the grate with the clippings, filters, &c., and *set fire to them from the top*. If ignition takes place from the bottom, the chances are that the draught will

be immoderately strong, and waft up the chimney some of the silver. Throw on all the papers, little by little, until they are reduced to a fine ash, carefully sweep up the ashes, and either add them to the contents of the "waste jar," or reserve them to mix with the precipitated Chloride after it has been dried.

It should have been mentioned with respect to the "waste jar" that it should not be too highly charged with common salt; because Chloride of Silver is, to some extent, soluble in concentrated solutions of Chloride of Sodium, and therefore a little waste might be incurred when drawing off the superfluous liquid. Care also should be taken to notice that all the Silver has been precipitated before drawing off the water. This is easily ascertained by adding a drop of solution of Chloride of Sodium to the liquid. If all the precious metal has not been precipitated a decided cloudiness will be apparent.

3rd. Another saving of Silver arises from the fixing solutions of Hyposulphite of Soda. This economy is seldom practised, for the reasons that the operation is a very disagreeable one, and as it is the custom now-a-days to use fresh solutions for every batch of prints fixed, the resulting proceeds are scarcely worth the trouble of recovering them.

Silver is reduced from these used solutions by means of Liver of Sulphur (Sulphide of Potassium). The form in which the Silver is precipitated is that of an impure Sulphide containing a great excess of Sulphur. But this operation must be conducted at a distance from the dark room, else the sulphurous fumes which are given off would be very prejudicial both to health, and more particularly to clean and clear Photographic manipulation.

4th. *Recovery of Gold.*—When the toning bath has apparently become exhausted and refuses to tone any more prints, it still contains a considerable quantity of Gold which has become *inert*. To precipitate this, throw in a little of a solution of Protosulphate of Iron. The black deposit which is immediately formed consists mainly of Carbonate and Oxide of Iron mixed with metallic Gold in an extremely fine state of division. Filter. The precipitate remains in the filter, which should be dried and burnt along with the silver filters. It is not worth while to keep these wastes separate, as the refiner allows for

the Gold when reducing the whole, and can estimate the value very accurately.

When the time has come to clear the "waste jar" of its Chloride or other insoluble salt of Silver, all the clear water is drawn off with a syphon, the moist precipitate is spooned out into a large evaporating basin, or into one of those *enamelled* iron pots or pans which can now be purchased at most of the ironmongers' shops and the water driven off by heat.

All these "wastes," *when dry*, may be reduced together, and by any one who has competent metallurgical knowledge, and who is in possession of a furnace specially fitted for the work; but from the Writer's experience, by far the best plan is to send the wastes to the professional refiner, who after recouping himself for his trouble, will show more of the precious metal than one who only works occasionally can possibly do.

REMOVAL OF SILVER STAINS FROM THE HANDS, LINEN, ETC.

The black stains upon the hands caused by Nitrate of Silver may readily be removed by rubbing them with a moistened lump of Cyanide of Potassium, leaving it on the hands for a little time, and then washing well with water. A solution of Iodide of Potassium allowed to dry on the hands will also, after a time, change the black stains into yellow Iodide of Silver, which may then be removed by Hyposulphite of Soda.

Stains upon white linen may be easily removed by brushing them with a solution of Iodine in Iodide of Potassium, and afterwards washing with water and soaking in Hyposulphite of Soda, or Cyanide of Potassium, until the yellow Iodide of Silver dissolves out; the Bichloride of Mercury (neutral solution) also answers well in many cases, changing the dark spot to white.)

The following liquid, when other means fail, is an energetic remover of Silver stains :—Cyanide of Potassium, 100 grains; Iodine, 10 grains; Water, 1 ounce: the solution should be colourless.

MODE OF TAKING THE SPECIFIC GRAVITY OF LIQUIDS.

Instruments are sold, termed "Hydrometers," which indicate specific gravity by the extent to which a glass bulb

containing air, and properly balanced, rises or sinks in the liquid; but a more exact process is by the use of the specific gravity bottle.

The bottles are made to contain exactly 1000 grains of distilled water, and with each is sold *a brass weight*, which counterbalances it when filled with pure water.

In taking the specific gravity of a liquid, fill the bottle quite full and insert the stopper, which being pierced through by a fine capillary tube allows the excess to escape. Then, having wiped the bottle quite dry, place it in the scale-pan, and ascertain the number of grains required to produce equilibrium; this number added to, or subtracted from, *unity* (the assumed specific gravity of water), will give the density of the liquid.

Thus, supposing the bottle filled with *rectified Ether* to require 250 grains to enable it to counterbalance the brass weight,—then 1· *minus* ·250, or ·750, is the specific gravity; but in the case of *Oil of Vitriol* the bottle, when full, will be *heavier* than the counterpoise by perhaps 836 grains; therefore 1· *plus* ·836, *id est*, 1·836, is the density of the sample examined.

Sometimes the bottle is made to hold only 500 grains of distilled water in place of 1000: in this case the number of grains to be added or subtracted must be multiplied by 2.

The form of specific gravity bottle, now most commonly used, has a brass weight which counterpoises the empty bottle only. This is an advantage, because the weight indicated by the liquid, when the bottle is filled, at once indicates the specific gravity; or in the case of a bottle holding 500 grains of distilled water, the weight multiplied by 2 will indicate the sp. gr. The temperature should register 60° Fahr.

REMOVAL OF VARNISH FROM GLASS PLATES.

The black varnish may often be removed from Collodion positives by means of Chloroform or Benzol, neither of which dissolves the Pyroxyline constituting the film.

To remove the varnish from a collodion negative apply a weak solution of caustic potash in water, to which a little alcohol is added. The precise strength of the solution is im-

material, but the following may from long experience be recommended :—

Caustic potash . . .	1 ounce
Alcohol	10 ounces
Water	10 ,,

After the varnish is dissolved, wash under a gentle stream of water.

If the ultimate object be to detach the collodion film from the glass plate, it must next be placed in a ten per cent. solution of hydrochloric or acetic acid, care being taken not to damage the film when detached.

If the utilization of the glass plate be the only object, the best way of removing old varnished films is to place the plate in boiling water, to which has been added common washing soda. This loosens the film in about half a minute.

VARNISH FOR BLACKING BRASS-WORK.

Take the ordinary spirit-lacquer of the shops, and rub it up with vegetable black into a thin cream, afterwards filtering through muslin. The brass-work must be heated before this varnish is applied.

FORMULA FOR NEGATIVE VARNISH.

Sandarac	4 ounces.
Alcohol	28 ,,
Oil of lavender	3 ,,
Chloroform	5 drachms.

Another.

Tough, hard, and durable :—

Shellac	$1\frac{1}{4}$ ounce.
Mastic	$\frac{1}{4}$,,
Oil of turpentine	$\frac{1}{4}$,,
Sandarac	$1\frac{1}{4}$,,
Venice turpentine	$\frac{1}{4}$,,
Camphor	10 grains.
Alcohol	20 fluid ounces.

Another.

Sandarac	90 ounces.
Turpentine	36 ,,
Oil of lavender	10 ,,
Alcohol	500 ,,

Another.

This one may be rubbed down with powdered resin, and gives a splendid surface for retouching:—

Sandarac	2 ounces.
Seed lac	1 to 1½ ounce.
Castor oil	3 drachms.
Oil of lavender	1½ drachm.
Alcohol	18 fluid ounces.

NEGATIVE RETOUCHING VARNISH.

Sandarac	1 ounce.
Castor oil	80 grains.
Alcohol	6 ounces.

First dissolve the sandarac in the alcohol, and then add the oil.

GROUND GLASS VARNISH.

Sandarac	90 grains.
Mastic	20 ,,
Ether	2 ounces.
Benzole	½ to 1½ ounce.

The proportion of the benzole added determines the nature of the matt obtained.

SOLUTION FOR SILVERING GLASS MIRRORS (Martin's).

A.

Nitrate of silver	175 grains.
Distilled water	10 ounces.

B.

Nitrate of ammonia	262 grains.
Distilled water	10 ounces.

C.

Pure caustic potash . . . 1 ounce (avoirdupois).
Distilled water 10 ounces.

D.

Pure sugar candy ½ ounce (avoirdupois).
Distilled water 5 ounces.

Dissolve and add—

Tartaric acid 50 grains.

Boil in a flask for ten minutes, and when cool add—

Alcohol 1 ounce.

Distilled water *quant. suff.* to make up to 10 ounces.

For use take equal parts of A and B. Mix together also equal parts of C and D, and mix in another measure. Then mix both these mixtures together in the silvering vessel, and suspend the mirror face downward in the solution.

INTENSIFYING SOLUTION FOR GELATINE NEGATIVES.

(Edwards's).

Saturated solution of bichloride of mercury . 10 ounces.
Iodide of potassium 10 drachms.

Dissolve the iodide of potassium in ten ounces of water, and pour gradually into the mercurial solution until the precipitate thrown down is *nearly* redissolved. Add one ounce of hyposulphite of soda in crystals.

Another.

Mercury bichloride . . 60 grains in 4 ounces water.
Iodide of potassium . . 96 ,, ,, 2 ,, ,,
Hypo. 120 ,, ,, 2 ,, ,, Mix.

INTENSIFYING SOLUTION FOR GELATINE.

(Mr. William England's).

Mercuric chloride 20 grains.
Ammonium chloride 20 ,,
Water 1 ounce.

Wash the negative thoroughly after fixing, and apply the above until the film acquires a uniformly grey tint. Wash again and apply a very weak solution of ammonia, ten drops of the latter to an ounce of water.

TO RESTORE FADED NEGATIVES.

Mr. W. C. Debenham recommends the following solution for the purpose of restoring printing force to negatives which have faded after mercurial intensification:—

Schlippes' salt	10 grains.
Water	1 ounce.

Wet the film thoroughly by soaking in a dish of water, and immerse in the restoring solution until the desired effect is obtained.

TO REMOVE THE LAST TRACES OF HYPO FROM THE FILM.

Peroxide of hydrogen (twenty vols.) .	1 drachm.
Water	5 ounces.

After washing the negative well, it is immersed for a couple of minutes in the solution and again rinsed in water, when the intensification with silver can be at once proceeded with.

Another.

Where peroxide of hydrogen is not obtainable, the following may be used as a substitute, the solution containing that substance in combination with others:—

Barium dioxide	1 ounce.
Glacial acetic acid	1 ,,
Water	4 ounces.

Reduce the barium dioxide to a fine powder, and add it gradually to the acid and water, shaking until dissolved. A few minutes' immersion in this solution will effectually remove or destroy the last traces of hypo.

Another.

A simple plan, brought forward by Captain Abney for this specific purpose, consists in employing a saturated solution of

alum in place of the solution of hydroxyl or peroxide of hydrogen.

EAU DE JAVELLE.

Dry chloride of lime (hypochlorite of lime)	2 ounces.
Carbonate of potash	4 ,,
Water	40 ,,

Mix the chloride of lime with thirty ounces of water; dissolve the carbonate of potash in the remainder. Mix, boil, and filter.

COWELL'S CLEARING SOLUTIONS FOR GELATINE NEGATIVES.

Alum	2 ounces.
Citric acid	1 ounce.
Water	10 ounces.

Wash moderately after fixing, and immerse the negative in the above.

Another.

Saturated solution of alum	20 ounces.
Hydrochloric acid (commercial)	1 ounce.

Immerse the negative after fixing, having previously washed it for two or three minutes under the tap; wash well after removal from the alum and acid.

WEIGHTS AND MEASURES.

Troy or Apothecaries' Weight.

1 Pound = 12 Ounces. 1 Ounce = 8 Drachms. 1 Drachm = 3 Scruples. 1 Scruple = 20 Grains. (1 Ounce Troy = 480 Grains, or = 1 Ounce Avordupois *plus* 42·5 Grains.)

Avoirdupois Weight.

1 Pound = 16 Ounces. 1 Ounce = 16 Drachms. 1 Drachm = 27·343 Grains. (1 Ounce Avoirdupois = 437·5 Grains.) (1 Pound Avoirdupois = 7,000 Grains, or = 1 Pound Troy *plus* 2½ Troy Ounces *plus* 40 Grains.)

Imperial Measure.

1 Gallon = 8 Pints. 1 Pint = 20 Ounces. 1 Ounce = 8 Drachms. 1 Drachm = 60 Minims. (A Wine Pint of water measures 16 Ounces, and weighs a Pound.)

An Imperial Gallon of water *weighs* 10 Pounds Avoirdupois, or 70,000 Grains. An Imperial Pint of water *weighs* 1¼ Pound Avoirdupois. A fluid Ounce of water *weighs* 1 Ounce Avoirdupois, or 437·5 Grains. A fluid Drachm of water *weighs* 54·7 Grains. A Minim weighs 0·91 Grains.

French Measures of Weight.

1 Kilogramme = 1,000 Grammes = something less than 2¼ Pounds Avoirdupois.

1 Gramme = 10 Décigrammes = 100 Centigrammes = 1,000 Milligrammes = 15·433 English Grains.

A Gramme of water *measures* 1 Cubic Centimètre, or 17 English Minims, nearly. 1,000 Grammes of water *measure* 35½ English fluid Ounces.

French Fluid Measures.

The cubic centimètre usually represented by "c. c." is the unit of the French measurement for liquids. It contains nearly seventeen minims of water; in reality, it contains 16·896 mimims. The weight of this quantity of water is one gramme. Hence it will be seen that the cubic centimètre and the gramme bear to each other the same relation as our drachm for solids and the drachm for fluids, or as the minim and the grain. The following table will prove to be sufficiently accurate for photographic purposes :—

Cubic Centimètres.		Minims (as near as possible).		Oz.	drs.	mins.
1	=	17				
2	=	34				
3	=	51				
4	=	68	or	0	1	8
5	=	85	,,	0	1	25
6	=	102	,,	0	1	42
7	=	119	,,	0	1	59
8	=	136	,,	0	2	16
9	=	153	,,	0	2	33
10	=	170	,,	0	2	50
20	=	340	,,	0	5	40
30	=	510	,,	1	0	30
40	=	680	,,	1	3	20
50	=	850	,,	1	6	10
60	=	1020	,,	2	1	0
70	=	1190	,,	2	3	50
80	=	1360	,,	2	6	40
90	=	1530	,,	3	1	30
100	=	1700	,,	3	4	20

French Measures of Length.

1 Mètre = 10 Décimètres = 100 Centimètres = 1,000 Millimètres = 39·37079 English inches.

A metre is equivalent to the ten-millionth part of the arc of the meridian, extending from the Equator to the Pole.

The Conversion of French into English Weight.

Although a gramme is equal to 15·4346 grains, the decimal is one which can never be used by photographers ; hence in the following table it is assumed to be $15\frac{2}{5}$ grains, which is the nearest approach that can be made to *practical* accuracy :

Grammes.		Grains.		Drms.	grns.
1	=	$15\frac{2}{5}$			
2	=	$30\frac{4}{5}$			
3	=	$46\frac{1}{5}$			
4	=	$61\frac{3}{5}$	or	1	$1\frac{3}{5}$
5	=	77	,,	1	17
6	=	$92\frac{2}{5}$	,,	1	$32\frac{2}{5}$
7	=	$107\frac{4}{5}$	,,	1	$47\frac{4}{5}$
8	=	$123\frac{1}{5}$	,,	2	$3\frac{1}{5}$
9	=	$138\frac{3}{5}$	,,	2	$18\frac{3}{5}$
10	=	154	,,	2	34
11	=	$169\frac{2}{5}$	,,	2	$49\frac{2}{5}$
12	=	$184\frac{4}{5}$	,,	3	$4\frac{4}{5}$
13	=	$200\frac{1}{5}$	,,	3	$20\frac{1}{5}$
14	=	$215\frac{3}{5}$	,,	3	$35\frac{3}{5}$
15	=	231	,,	3	51
16	=	$246\frac{2}{5}$	,,	4	$6\frac{2}{5}$
17	=	$261\frac{4}{5}$	,,	4	$21\frac{4}{5}$
18	=	$277\frac{1}{5}$	,,	4	$37\frac{1}{5}$
19	=	$292\frac{3}{5}$	,,	4	$52\frac{3}{5}$
20	=	308	,,	5	8
30	=	462	,,	7	42
40	=	616	,,	10	16
50	=	770	,,	12	50
60	=	924	,,	15	24
70	=	1078	,,	17	58
80	=	1232	,,	20	32
90	=	1386	,,	23	6
100	=	1540	,,	25	40

INDEX.

Abnormal development, 142
Acetic acid, 29
Acids, 14
Acids and salts, 21
Albumen, 31
Albuminized paper printing, 318
Alcohol, 32
 methylated, 35
Alum, 36
American Rapid Lens, 418
Ammonia, 36, 145
 bichromate of, 37
 carbonate of, 38
 nitrate of, 39
Ammonium sulphide, 38
 bromide, 39
 chloride, 39
 iodide, 40
 sulphocyanide, 40
Aniline, 40
 process, 383
Aqua regia, 41
Argentometer, 321
Arsenic, bromide of, 41
Atomic theory, 19

Barium chloride, 41
Baryta, nitrate of, 42
Bases, 14
Benzole, 42
Binocular vision, 425
Bitumen, 43
Bleaching positives, 197
Bromides, testing purity of, 43
Bromine, 43

Cadmium, 44
 bromide, 44
 iodide, 45
Calcium bromide, 45
 chloride, 46
 iodide, 46
Camphor, 46
Canada balsam, 47
Caoutchouc, 47
Carbolic acid, 47
Carbon enlargements, 315
Carbon printing, 339
Castor oil, 47
Cellulose, different forms of, 158
Charcoal, animal, 48
Chemical action of various iodides, 174
Chemical changes, 23
Chlorine, 48
Chloroform, 49
Chromatic aberration, 402
Chromium, 50
Chromotype or Lambertype, 436
Citric acid, 50
Collodion, 151, 164
Collodion negatives, 198, 284
Collodion positives, 188, 281
Collodion transfers, 307
Collotype printing, 362
Combination by weight, laws of, 18
Compounds and mixtures, 13
Cyanogen, 51

Dark room, 263

Defects in prints, 331
Developed images, nature of, 139
Developer for positives, 193
Development of invisible image, 117
Distortion, its nature and cure, 412
Double decomposition, 25

Eau de Javelle, 457
Elementary bodies, tables of, 10
Engineers' plans, Willis's process for, 385
Enlargements, 302
Enlarging by artificial light, 313
Equivalent focus, how to ascertain, 445
Ether, 53

Fading of prints, 254
Ferrotypes, 188, 281
Ferrous oxalate, 61
Fixing agents, 145
Fixing prints, 248
Foci of lenses, 398, 406
Fused nitrate of silver for bath, 184

Gallic acid, 53
Gallic acid as a reducing agent, 119
Gelatine, 54
Gelatine emulsion process, 365
intensifying solution for, 455
negatives, Cowell's clearing solutions for, 457
negatives, intensifying solution for 455
Glass house, 296
Glycerine, 54
Gold, chloride of, 55
hyposulphite of, 56
Gums, 56

Historical sketch of photography, 1

Hydriodic acid, 57
Hydrobromic acid, 57
Hydrochloric acid, 58
Hydrogen, peroxide of, 58
Hydrosulphuric acid, 58
Hypo., to remove last traces of, 456

Invisible image, nature of, 124
development of, 128
produced by ozone, 139
Iodide of silver, causes affecting sensitiveness of, 132
Iodine, 59
Iodizing solutions, 170, 265
Iron, acetate of, 60
ammonio-citrate of, 60
ammonio-sulphate of, 61
oxalate of, 61
protosulphate of, 62, 121
protonitrate of, 121
perchloride of, 62
iodide of, 63
Iron salts as reducing agents, 120

Kaolin, 63

Lead, acetate of, 64
Lenses, various forms of, 397
Light, action of, on chloride of silver, 110, 112
Light, action of, on organic silver compounds, 109, 113
Light, nature of, 392
properties of, 394
Lime, chloride of, 64
Lithium, iodide of, 65
Litmus, 65

Magnesium, 66
Mercury, chloride of, 66
Micro-photography, 388
Moser's researches on invisible images, 135

Naphtha, 67
wood, 35

Negative developers, 209
Negative solutions, formulæ for, 265
Negatives, to restore faded, 456
Nitrate bath, 268
Nitrate bath, chemistry of, 178
Nitric acid, 67
Nitrogen, 69
Nitro-glucose, 70
Nitro-hydrochloric acid, 70
Nitro-sulphuric acid for preparing pyroxyline, 155
Nomenclature of compounds, 20

Optics of photography, 392
Organic substances, chemistry of, 26
matter, 71
Orthoscopic lens, 414
Outlines of general chemistry, 9
Oxygen, 71
Ozone, 72

Phosphoric acid, 72
Photo block printing, 361
Photo-crayons, 312
Photo-lithography, 348
Plain paper printing, 316
Platinotype printing, 333
Portrait lenses, 421
Portraiture, 296
Positive and negative photographs, 186
Positive printing, 219, 316
Potash, 73
bichromate of, 74
carbonate of, 74
nitrate of, 75
oxalate of, 77
permanganate of, 77
Potassium, bromide of, 75
cyanide of, 76, 148
fluoride of, 76
iodide of, 77, 172
sulphide of, 78
Pyrogallic acid, 79
Pyroxylic spirit, 35
Pyroxyline, 79

Rapid rectilinear lens, 418
Reducing agents, action on invisible image, 117
Reducing agents, substances employed as, 118
Refraction of light, 395
Removal of varnish from negatives, 452
Residues, saving of, 449

Salts, 16
Silver, 80
acetate of, 81
albuminate of, 81
ammonio-nitrate of, 82
bromide of, 82
carbonate of, 83
chloride of, 83, 104
citrate of, 83
fluoride of, 84
hyposulphite of, 84
iodide of, 84, 106
nitrate of, 85, 102
nitrite of, 87
oxide of, 88, 107
sulphide of, 88
Silver salts, chemistry of, 102
properties of, 108
Silvering glass mirrors, solution for, 454
Single landscape lens, 408
toning and fixing bath, 241
Soda, acetate of, 89
carbonate of, 89
citrate of, 89
hyposulphite of, 90, 146
phosphate of, 90
sulphite of, 91
Sodium, aurochloride of, 91
chloride of, 92
Solar camera enlargements, 304
Specific gravity of liquids, 451
Spherical aberration, 404
Spontaneous decomposition in pyroxyline, 163
Stains, removal of, 451
Stannotype, the, 360

Stereoscopic photography, 425
Storing negatives, 294
Sulphocyanides, 93
Sulphuretted hydrogen, 93
Sulphuric acid, 93
Symbols of compounds, 11

Tannin, 95
Tartaric acid, 96
Testing permanence of prints, 261
Testing silver solutions, 447
Tetrathionic acid, 96
Toning by gold, 240
Toning by sulphur, 240
Transparencies in carbon, 347
Triple achromatic lens, 415
Turmeric, 97

Uranium, nitrate of, 98

Varnish, for blacking brass work, 453
ground-glass, 454
negative, formulæ for, 453
negative retouching, 454
removal of, from glass plates, 452
Varnishing negatives, 292
Vocabulary of photographic chemicals, 29

Water, 98
Weights and measures, 458
Wet collodion, manipulations of, 274
Wide angle lenses, 419
Wood blocks, printing on, 346
Woodburytype, 356

Zincography, 352

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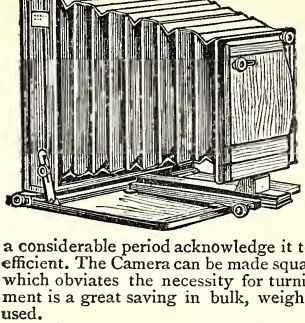
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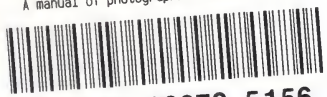
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